
Molecular Mechanics (MM4) Calculations on Conjugated Hydrocarbons*

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ABSTRACT

The MM4 force field has been extended to conjugated hydrocarbon systems. It retains most of the formalism and computational schemes that were present in MM3. Several cross-terms have been added in MM4 that were not present in MM3, mainly to improve vibrational frequencies, but also to improve structures and energies. Additional bond order dependence equations have been included. About 80 molecules have been examined, some in multiple conformations, and others with more complete experimental profiles. Conformational energy differences/barriers are generally fit to within 0.5 kcal/mol unless they are very large. The MM4 method for calculating heats of formation has been modified to include vibrational as well as steric energy contributions. The heats of formation for 35 alkenes and 57 conjugated hydrocarbons were determined to have an overall root mean square (rms) deviation of 0.68 kcal/mol from experiment (0.47 kcal/mol weighted rms). The vibrational frequency rms error for eight conjugated hydrocarbons is 31 cm⁻¹. Geometries are fit for the most part to within the following ranges: 0.004 Å for bond lengths, 1° for bond angles, 4° for torsion angles, and 0.5% for moments of inertia (r_z). © 1996 by John Wiley & Sons, Inc.

Introduction

The goal of MM4¹ is to simultaneously fit geometries, energy barriers, conformational energies, heats of formation and other thermody-

namic quantities, and vibrational frequencies.[‡] This should occur without a disruption to the force field's integrity. In other words, all the equations and cross-terms that comprise the force field should have clear physical meanings within it. However,

[‡] Bond lengths are in Å, angles are in degrees, and energies are in kcal/mol, except for "spectroscopic constants," where stretching is in mdyne/Å, and bending is in mdyneÅ/rad,² and torsion is kcal/mol. The off-diagonal units obtained by multiplying 2 or more of the above have units corresponding to such multiplication unless otherwise stated.

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the improvements obtained by any equation or cross-term in one domain should not be offset by unrealistic changes in another. For instance, if one improves frequencies for benzene, it should not come at the expense of butadiene's energy barrier. Thus, the new equations in MM4 and the relevant parameters have been optimized such that the calculated MM4 results lead to several significant improvements over MM3, especially for the vibrational frequencies, without anything already calculated well by MM3 getting significantly worse.

Although MM3 has treated geometries, conformational energies, and heats of formation reasonably well for conjugated hydrocarbons, problems still remained, especially for the vibrational frequencies. For a more complete discussion of the new MM4 cross-terms, refer to the previous article.² As outlined in this article, some additional cross-terms have been added, including bend-torsion-bend, torsion-improper torsion-improper torsion, and stretch-stretch terms, which now improve coupled in-plane bending, out-of-plane bending, and stretching vibrational frequencies, respectively. Most of the details concerning the MM4 alkene and conjugated hydrocarbon vibrational frequencies are discussed in the following article.³

Treating conjugated hydrocarbons, especially with respect to alkenes, is not completely straightforward. Although alkene and conjugated hydrocarbon systems both have the same atom type (type 2) to represent the sp^2 hybridized carbon, conjugated systems cannot be simply treated by standard classical molecular mechanics, since bond lengths, stretching frequencies, and energy barriers depend on pi-bond orders (p_{ij}). For example, benzene has equivalent bond lengths ($p_{ij} \approx 0.67$), while butadiene has two short terminal bonds ($p_{ij} \approx 1$) and a longer central bond ($p_{ij} \approx 0.26$), which correspond to its pattern of pi-bond orders. If $C_{sp^2}-C_{sp^2}$ bond parameters (k_s, l_0) were chosen to fit the bond lengths of benzene, the bond lengths in butadiene would also be calculated to be of approximately equal length (similar to benzene). Thus, in MM3 a pi-system molecular orbital treatment was used in the molecular mechanics calculation.⁴ A variable electronegativity self-consistent field (VESCF) calculation^{4,5} is first carried out on the planar pi-system, and pi-bond orders are determined for conjugated bonds. If the conjugated part of the molecule is nonplanar, it is planarized before the VESCF calculation takes place. In MM3, the bond stretching and natural bond length (k_s and l_0) and the V2 torsional parameters are bond-order dependent for conjugated systems, and this

dependence is carried over into MM4. It became clear that bond-order dependence in other torsion equations would be necessary to better fit to experiment, and thus additional bond-order-dependent equations have been introduced into MM4 and will be discussed in this article.

At this point it is important to note that in some instances the VESCF calculation may give results which are slightly dependent on the choice of starting geometry (although the final energies of the "different" optimized structures are usually within 0.1 kcal/mol of each other). A VESCF calculation is carried out on the initial geometry in order to calculate the electronic energy and determine bond orders, and this is followed by either a block-diagonal or full-matrix optimization.⁴ If a significant change in geometry occurs, another VESCF calculation is undertaken and the molecule is optimized again. This procedure occurs iteratively until overall consistency is achieved.⁸ However, the VESCF calculation is carried out in single precision (with a 32-bit word), and thus this part of the calculation does not always converge to limits as tight as those for the rest of the calculation.

Results and Discussion

CONFORMATIONAL ANALYSIS: ENERGY BARRIERS AND DIFFERENCES

First, it should be stated that the force fields for alkanes¹ and for alkenes² are carried over to this work intact. No changes were made—only additions that are specific for conjugated systems. Bond-order-dependent equations will be discussed as well as their effects on rotational barriers. The following compounds are also discussed in some detail this section: 1,3-butadiene, isoprene (2-methylbutadiene), 2,3-dimethylbutadiene, styrene, 1,3-cycloheptadiene, 1,3,5-cycloheptatriene, 1,3,5,7-cyclooctatetraene, 4,5-dimethylphenanthrene, and corannulene.

BOND-ORDER-DEPENDENT EQUATIONS

To fit the butadiene, cycloheptatriene, cyclooctatetraene, and corannulene barriers simultaneously to experiment and *ab initio* calculations while also keeping the out-of-plane bending frequencies for conjugated compounds, especially benzene, close to experiment, a V3 bond-order-dependent equation was introduced [see eq. (1)].

⁸ See later discussion in connection with Fig. 9c.

$$V_3 = K_{V_3}[1 - p_{ij}(\omega)] * V_3^\circ \text{ for any central } C_{sp^2}-C_{sp^2} \text{ bond,}$$

$$K_{V_3} \text{ equals } 1.25, p_{ij}(\omega) \text{ is the bond order about bond } i-j \text{ for torsion } \omega \quad (1)$$

Since the V_3 term for the torsional potential is thought of as a steric factor, central bonds with pi-bond orders of 1 would not be expected to have a V_3 contribution; bonds with bond orders less than 1 could be expected to have progressively increasing contributions of V_3 , which eq. (1) adjusts linearly. In other words, the less double bond character a particular torsion contains, the greater the V_3 contribution. Note that for conjugated systems, the type $C_{sp^2}-C_{sp^2}-C_{sp^2}-C_{sp^2}$ (2-2-2-2) V_3 term is set to zero, while the type $C_{sp^2}-C_{sp^2}-C_{sp^2}-C_{sp^3}$ (2-2-2-1) and $C_{sp^2}-C_{sp^2}-C_{sp^2}-H$ (2-2-2-112) V_3 terms have negative values. This, in effect, changes the energies of nonplanar compounds relative to their planar counterparts and damps out the V_3 effects on out-of-plane bending frequencies for benzene, while still allowing heats of formation to be fit reasonably well. The logic is similar to the adjustment for V_2 with bond order as in butadiene derivatives,⁶ which MM3 already takes into account. In both MM3 and MM4, the V_2 term is adjusted according to the degree of conjugation by eq. (2).

$$V_2 = [A + p_{ij} * \beta_{ij}]V_2^\circ,$$

where p_{ij} is equal to the bond order
about bond $i-j$ (at $\omega = 0^\circ$) and β_{ij}
is the resonance integral

$$(2)$$

The coefficient A equals -0.06 in MM3 and -0.09 for MM4. This coefficient, in effect, lowers the V_2 term relatively more about dihedral angles whose central diene bonds have lower bond orders.

Thus, lower double bond character (p_{ij}) involves a lower V_2 and an increased V_3 contribution in contrast to a double bond with higher bond order, where the reverse would be expected. Unfortunately, this is not a direct way of dealing fully with the electronic effects in the conjugated systems. However, incorporating bond order dependence into the torsional parameters improves the overall results of the force field compared to when this dependence is neglected, and it is physically reasonable. The torsion-torsion cross-term, which was discussed earlier,¹ also involves this dependence.

To calculate the diene (e.g., isoprene and *trans*-penta-1,3-diene) and aromatic (e.g., hexamethylbenzene) methyl rotational barriers correctly, the 5-1-2-2 V_3 torsional term needed to be bond order dependent, according to eq. (3).⁷ This equation was included in the MM2 program but was accidentally left out of MM3. It has now been reintroduced into MM4.

$$V_3(5-1-2-2) = p_{ij}V_3^\circ(5-1-2-2) + (1 - p_{ij})V_3(5-1-2-1), \text{ where}$$

p_{ij} is the bond order about bond $i-j$

$$(3)$$

In conjugated systems, the 5-1-2-2 V_3 term does not retain the original value (5-1-2-2 V_3°) in the parameter list. Instead, it is adjusted by eq. (3) such that when the $C=C$ bond has mostly double bond character ($p_{ij} \sim 1$), the 5-1-2-2 V_3 term will basically retain its normal value. This favors structures in which a hydrogen eclipses the double bond. When the $C=C$ bond has more single bond character, the single bond term (1-2-1-5 V_3) will have a larger contribution to the 5-1-2-2 V_3 term, and this term will be calculated more positive. In the case of toluene, where the bond orders are equal on either side of the methyl group, the V_3 terms will be equal and the torsional contribution to the rotational barrier will be zero. Some results are shown in Table I.

The conformational energy differences and rotational barriers for selected conjugated hydrocarbons are reported in Tables II-VI.

1,3-Butadiene

This molecule has been studied by electron diffraction,^{11,12} Raman,^{13,14} IR,¹⁵ and ultraviolet (UV)¹⁶ experimentally and also by *ab initio* calculations.^{17,18} Although the *trans* form was shown to predominate strongly by both experiment and cal-

TABLE I.
Energy Barriers to Methyl Rotation in Conjugated Systems (kcal / mol).

	Experiment	MM4
<i>trans</i> -Isoprene	2.62 ^a , 2.71 ^b	2.53
<i>trans</i> -Penta-1,3-diene	1.80 ^c	1.70

^a See ref. 8, microwave.

^b See ref. 9, infrared (IR) exp. fits V_3 .

^c See ref. 10, microwave.

ulation, the geometry of the *cis* conformer remains unclear. In a 1975 Raman experiment, Carrera presented evidence that *cis*-butadiene (planar) was a minor form, with a local minimum about 2–2.5 kcal/mol above the *trans*-conformer.¹³ He used MM2 structures to analyze the spectrum. Bock and co-workers reanalyzed the Raman spectrum in 1979 and concluded that the spectrum was more consistent with a *gauche* structure.¹⁴

A gas-phase IR study/normal coordinate analysis on d_0 , d_4 , and d_6 butadiene led Furukawa and coauthors to conclude that the second stable conformer was probably *gauche*, although they mentioned that it would be reasonable to use the *cis* form "as a practical model."^{15a} However, an IR study by Fischer and Michl in an argon matrix concluded that the *cis* form was the second low-energy conformer.^{15b} as did an IR/UV study by Squillacote and co-workers (also in an argon matrix).^{16a} A high-temperature UV experiment by Mui and Grunwald led to the conclusion that the *cis*/*gauche* potential well is basically one and the same (i.e., the *cis* is a small bump between the *gauche* conformers, well below the first vibrational level).^{16b}

Ab initio calculations carried out on *cis*- and *gauche*-butadiene at increasing levels of theory (from SCF, CCSD, and CISD [+Q] with DZ, DZd, and DZP basis sets) suggested the presence of a *gauche* minimum energy conformer, with the *cis* existing as a transition state 0.38–0.64 kcal/mol above the *gauche*.¹⁷ An MP3/6-311 + G**/MP2/6-31G* calculation after correction for zero-point energies gives a larger energy difference of 0.85 kcal/mol in favor of the *gauche*.¹⁸ Most experimental results do not rule out the presence of a local *gauche* structure with a torsion angle of up to about 15°,^{15,16} while *ab initio* results predicted the *gauche* structure to have a torsion angle of about 40°.

It is important to note that the MM4 parameters were not chosen to fit any butadiene results explicitly. When all of the conjugated hydrocarbon data were considered, the MM4 results for butadiene came out to be more in line with the Mui and Grunwald findings. Using the MM4 computed final (potential + electronic) energies, the *cis* form is calculated to have one negative eigenvalue and is 2.54 kcal/mol above the *trans* conformer; the *gauche* structure has a dihedral angle of 11.6° about the central butadiene bond and is a minimum. Although the *cis* has one negative eigenvalue, it is actually calculated 0.004 kcal/mol lower in energy than the *gauche* conformer (this is below

the limit of accuracy of the method). This discrepancy is due to the fact that the Newton-Raphson optimization determines the potential (steric) energy of the *cis* to be 0.007 kcal/mol higher, but the VESCF calculation determines the electronic energy of the *cis* (which is subsequently added) to be 0.011 kcal/mol lower than the *gauche* conformer.

Note that the results here are not straightforward to interpret. The MM4 *gauche* form is calculated to be *dl*, but because the vibrational level is above the *cis*, it is not. Thus, the 1.377 eu entropy of mixing contribution must be subtracted from the calculated value to obtain the MM4 entropy of the *gauche* form. The thermodynamic properties are rather dependent on the exact value of the lowest frequency (the MM4 value is 60 cm⁻¹). In the absence of other information, this value is used. Hence, the MM4 result seems to indicate that the *cis* conformer is a minor bump on the potential surface, and when the vibrational motion is included, it is the second low-energy structure. The barrier to rotation at 90° is calculated by MM4 to be 6.94 kcal/mol, compared with 7.16 kcal/mol by experiment.¹³

The weight of the experimental evidence, in our view, indicates that the *cis* conformation is just that, although the argon matrix may be forcing that geometry in one case. The *ab initio* evidence unambiguously indicates a *gauche* form. The potential well is, however, less than 1 kcal/mol in depth. It is therefore unclear, in our view, which picture is correct. We note, however, that when the torsional vibrational motion is included, the molecule is either planar or within a few tenths of a kilocalorie of planar.

The rotational barrier of butadiene from 0° to 180° has been calculated at 15° increments using the 6-31G** basis set at the Hartree-Fock and Møller-Plesset (MP2) levels of theory.¹¹ Stationary points at minima and maxima were optimized after releasing the torsional constraints. They were verified as minima and transition states by frequency calculations. Comparisons of HF, MP2, MM3, and MM4 results are shown in Table II. MM3 energies are "final energies," which include both steric and electronic energies. The MM4 and MP2/6-31G** (no vibrational [zero-point] energy corrections) results are also presented in a rotational profile (Fig. 1).

¹¹ All *ab initio* calculations (optimized at the 6-31G*/MP2 level) were carried out with Gaussian92 (see ref. 33), unless otherwise stated.

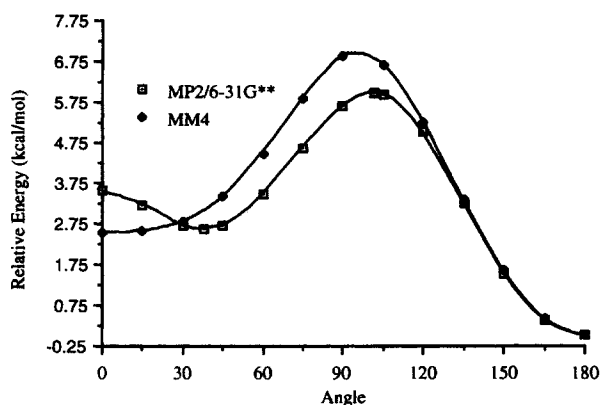


FIGURE 1. Rotational barrier for butadiene.

Isoprene

The only experimental results for this compound are Raman spectroscopy refined HF/3-21G data.¹⁹ HF/6-31G** and MP2/6-31G** results are reported in Table II. Again, as in butadiene, the general *ab initio* trends seem to be followed by MM4 (less well by MM3). Also, a ΔG^\ddagger of 3.9 ± 0.1 kcal/mol for the conversion *gauche*- to *trans*-conformer has been reported by Squillacote and co-workers.²⁰

2,3-Dimethylbutadiene (DMB)

Squillacote and co-workers reported IR and Raman spectra for the major (*trans*) and minor (*gauche*) conformers.²⁰ They froze a hot gaseous mixture of these forms onto a cold CsI window and then measured the rate of decay of two bands in the UV spectrum (1/1000 DMB/argon matrix) upon warming. They reported a ΔG^\ddagger of 3.4 ± 0.1 kcal/mol for the conversion of the *gauche*- to the *trans*-conformer. In addition, the K_{eq} for the *gauche*/*trans* pair was determined from the peak heights of two additional bands in the spectrum (also in an argon matrix), and this gave a ΔG° of 1.7 ± 0.2 kcal/mol. The MM4 ΔG values are 0.7 kcal/mol for the *gauche*/*trans* energy difference and 1.8 kcal/mol for the barrier to conversion, which are lower than the experimental results. However, the final (potential + electronic) energy differences are 2.0 and 3.5 kcal/mol, respectively, which are larger than the *ab initio* values. The MM4 ΔG values are lowered due to the vibrational energy and entropy of mixing (two *gauche* forms). The final energy differences include the electronic energies calculated by the VESCF cycle

TABLE II.
Energy Barriers and Differences for Butadiene, Isoprene, 2,3-Dimethylbutadiene, and Styrene (kcal / mol).

Compound	Conformer	Exp.	Ref.	HF / 6-31G**	MP2 / 6-31G**	MM3	MM4 ^a
Butadiene ^b	<i>trans</i>	0		0	0	0	0
	<i>cis</i>	2.49		3.88	3.55	1.85	2.54
	<i>cis-gauche</i>	—		+0.88	+0.93	-0.50	-0.01 ^c
	~ 90°	7.16	13	6.06	5.97	7.42	7.06
Isoprene ^d	<i>trans</i>	0		0	0	0	0
	<i>cis</i>	3.38		3.59	3.59	1.67	3.09
	<i>gauche</i>	2.65		2.34	2.27	1.66	2.86
	(diene angle)	(39.2°)		(43.0°)	(41.2°)	(8.2°)	(30.0°)
	~ 90°	5.78	19	5.21	5.36	5.44	5.81
2,3-Dimethyl- butadiene	<i>trans</i>	0		0	—	0	0
	<i>gauche</i>	1.7 ^e		1.4	—	1.3	0.7 ^g / 2.04
	~ 90°	3.4 ^f	20	3.0	—	3.2	1.8 ^g / 3.52
Styrene	<i>gauche</i>	—		—	—	—	0
	<i>cis</i>	0		—	—	0	+0.001
	~ 90°	1.78 ^h / 2.88 ⁱ	21 / 22	—	—	3.88	3.75

^a The MM4 results are final (potential / steric + electronic) energies unless otherwise noted.

^b Raman study (potential energy difference).

^c See butadiene section for explanation of this value.

^d *Ab initio* refined Raman data (potential energy difference).

^e These values are from a UV study (ΔG°).

^f These values are from a UV study (ΔG^\ddagger).

^g These MM4 results are ΔG .

^h Raman study (potential energy difference).

ⁱ HF / 6-31G* calculation.

and do not include the vibrational or entropy of mixing contributions.

Styrene

The minimum energy conformer for styrene has been assumed to be planar, but this is not certain. *Ab initio* calculations at the SCF level with 4-21G, 6-31G, and 6-31G* basis sets have shown the low-energy structure to be twisted 15–20° about the diene portion of the molecule.²³ Another *ab initio* study at the HF/6-31G* level of theory determined the 0° and 90° rotational barriers to be 0.04 and 2.88 kcal/mol, respectively.²² The gauche conformer was the minimum with a twist of 15.0°. A Raman study by Carierra reports the minimum energy structure as planar and a 90° barrier height of 1.78 kcal/mol.²¹ MM3 predicts a planar (cis) minimum, but MM4 calculates it to be twisted by 13.2°, with the planar molecule occurring as an insignificant bump (0.001 kcal/mol) on the potential surface. The barrier from the minimum to the 90° transition state is calculated by both MM methods to be approximately 4 kcal/mol. These results (see Table II) are higher than the experimental (2 kcal/mol) and *ab initio* (3 kcal/mol) results.

1,3-Cycloheptadiene

The minimum energy structure for cycloheptadiene has been postulated to exist in either a semiplanar (C_s) or twisted (C_2) conformation. Electron diffraction²⁴ and microwave²⁵ experiments indicate the C_s conformer, while nuclear magnetic resonance (NMR)²⁶ results favor a C_2 structure. To gain insight into these conflicting results, Hartree-Fock (HF) and MP2 calculations were carried out with the 6-31G** basis set. The HF result shows that the C_2 conformer lies 2.5 kcal/mol above the C_s , while the MP2 results puts the C_2 conformer 0.3 kcal/mol below the C_s .²⁷ These calculations indicate that the C_2 conformation may be present along with the C_s conformer. The MM4 result favors the C_s conformer by 2.2 kcal/mol (Table III).

Cycloheptatriene (CHT) and Cyclooctatetraene (COT)

The results for these compounds are presented in Table III. Cycloheptatriene is calculated by MM3 to be much too planar (final energy difference of 1.3 kcal/mol), and the free energy of activation (ΔG^\ddagger) to inversion is 2.3 kcal/mol, which is much

TABLE III.
Energies for Cycloheptadiene, Cycloheptatriene, and Cyclooctatetraene (kcal/mol).

Compound	Conformer	Exp.	Ref.	MM3	MM4
Cycloheptadiene	C_s	0		0	0
	C_2	2.5, -0.3 ^a	27	3.2	2.2 ^d
Cycloheptatriene	boat	0		0	0
	planar	5.7 ^b	28	1.3	3.4 ^e
Cyclooctatetraene	tub	0		0	0
	planar	13.7 ^c	29	14.2	13.5 ^f

^a The energy difference results are *ab initio* HF and MP2, respectively (6-31G** basis set).

^b NMR experiment (ΔG^\ddagger at 103 K).

^c NMR experiment (ΔG^\ddagger at 263 K).

^d MM4 value is a final energy difference.

^e MM4 value is ΔG^\ddagger at 103 K.

^f MM4 value is ΔG^\ddagger at 263 K.

lower than the reported ΔG^\ddagger of 5.7 ± 0.1 kcal/mol at 103 K.²⁸ As discussed in the previous article,² MM3 was parameterized for final energies only, regardless of experiment. Thus, the potential energy difference was always used for comparison with experiment, although other thermodynamic quantities (ΔH , ΔG) can be calculated with MM3. The MM4 structure is less planar and the calculated ΔG^\ddagger is 3.4 kcal/mol, higher than the MM3 value but still lower than experiment. The errors in the calculated structures, both bond angles and moments of inertia, also suggest that CHT is calculated too planar by MM4, although less so than by MM3. Attempts to improve this structure or barrier result in deviations from experiment for other compounds which share CHT's parameters, including 1,4-pentadiene and norbornadiene (geometry and heat of formation) and 1,4-cyclohexadiene, 9,10-dihydrophenanthrene, and 1,1-diphenylethane (heat of formation).

The final energy difference for the cyclooctatetraene (COT) inversion barrier is calculated to be 14.2 kcal/mol by MM3, while the ΔG^\ddagger is 17.1 kcal/mol. The MM4 and experimental ΔG^\ddagger (NMR at 263 K)²⁹ values are determined to be 13.5 kcal/mol and 13.7 kcal/mol, respectively. Again, the final energy differences are best used for comparison to experiment with MM3.

Biphenyl and Other Compounds

Table IV gives the MM4 results for some additional compounds previously examined with MM3. For biphenyl, experimental data are available which fit the torsional IR frequency to a V2/V4 torsional potential,³⁰ and thus the MM4 steric en-

TABLE IV.
Energy Barriers and Differences for Conjugated Hydrocarbons (kcal / mol).

Compound	Conformer	Exp.	Ref.	MM3	MM4
Biphenyl	twist (-41.5°)	0		0	0
	planar	1.4 ^a	30	2.52	2.47 ^b
	90°	1.6 ^a	"	1.10	1.85 ^b
1,3-Cyclohexadiene	nonplanar	0		0	0
	planar	3.1 ^c	31	2.46	3.4 ^d
1,2-Diphenylethane	trans	0		0	0
	gauche	> 0.0 ^e	32	0.34	0.05 ^b
1,2-Diphenylpropane ^f	gauche, anti	0		0	0
	anti, gauche	0.23 ^c	34	0.28	0.37 ^d
	gauche, gauche	0.82 ^c	"	0.94	1.27 ^d
	s-trans	0		0	
2,2-Metaparacyclophane	perpendic.	20.6 ± 0.3 ^c	35	20.0	21.4 ^d

^a IR experiment.^b MM4 value is determined from final (steric) energies.^c NMR result (ΔG^\ddagger).^d MM4 value is ΔG^\ddagger .^e IR / Raman experiment.^f g:me-ph, anti:ph-ph; anti:me-ph, g:ph-ph; g:me-ph, g:ph-ph.

ergy differences are used for comparison (see Table IV).

4,5-Dimethylphenanthrene

The activation energy barrier (ΔG^\ddagger) for racemization of 4,5-dimethylphenanthrene was found by experiment to be 16.1 ± 1.5 kcal/mol at 298 K from circular dichroism spectroscopy.³⁶ The transition state calculated by MM4 is bowl shaped with atoms 4,5,12,13,15,16 coplanar, and the ΔG^\ddagger is 18.1 kcal/mol. However, the bending constant, K_b , for the angle with atom types 1-2-2 (type 1) is different than for type 2.[†] The values for these bending constants are 0.38 and 0.68 md Å/rad² for types 1 and 2, respectively. The lower bending constant was needed for the type 1 angle to reduce the ΔG^\ddagger

[†] Type 1 bond angles have no hydrogens attached to the central atom in the angle ($-\text{CR}_2-$), whereas type 2 angles have one hydrogen attached to the central atom ($-\text{CRH}-$).

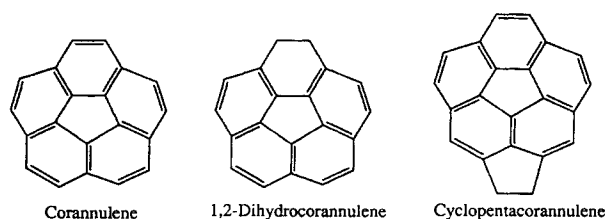
for 4,5-dimethylphenanthrene, although some frequencies which are dependent on this constant are calculated too low, while the larger constant for type 2 is mainly needed to reproduce experimental IR bending frequencies. The experimental ΔG^\ddagger for 3,4,5,6-tetramethylphenanthrene was determined to be 23.1 ± 0.5 . MM4 calculates this barrier to be 22.5 kcal/mol, which is closer to experiment than for the dimethyl analog. The results are presented in Table V.

Corannulene, 1,2-Dihydrocorannulene, and Cyclopentacorannulene

Calculated and experimental results for corannulene, 1,2-dihydrocorannulene, and cyclopentacorannulene (see Fig. 2) are presented in Tables VI and VII. The energy barrier to ring inversion (ΔG^\ddagger , bowl vs. planar) for corannulenyldimethylcarbinol, which is corannulene with an isopropanol sub-

TABLE V.
NMR Experimental (ΔG^\ddagger), MM3 (final energy), and MM4 (ΔG^\ddagger) Calculated Energy Barriers for 4,5-Dimethyl- and 3,4,5,6-Tetramethylphenanthrene (kcal / mol).

Compound	Conformer	Exp.	Ref.	MM3	MM4
4,5-Dimethylphenanthrene	nonplanar	0		0	
	planar	16.1 ± 1.5	36	17.4	18.1
3,4,5,6-Tetramethylphenanthrene	minimum	0			
	TS	23.1 ± 0.5	36	20.4	22.5

**FIGURE 2.** Corannulene structures.

stituent, has been determined by NMR at 209 K to be 10.2 kcal/mol.³⁷ The MM4 calculated ΔG^\ddagger for corannulene itself is 11.2 kcal/mol, while the MM3 result is 12.4 kcal/mol at this temperature. An experimental barrier for corannulene of 11–12 kcal/mol³⁸ has been reported, as well as *ab initio* values of 11.4 kcal/mol by local density functional theory (LDF),³⁷ 8.8 kcal/mol by HF/6-31G*,³⁸ and 14.3 kcal/mol by MP2/6-31G.³⁸

The MM4 inversion barrier for dihydrocorannulene is calculated lower (6.7 kcal/mol) than experiment and theory (see Tables VI and VII). This may be due to the low 1-2-2 type 1 bending force constant that was needed to reproduce the experimental activation energy barriers for 4,5-dimethyl- and 3,4,5,6-tetramethylphenanthrene, as mentioned in the previous section.

Two cross-terms in the MM4 force field have counteracting effects on the energy and structure of corannulene molecules. The torsion-torsion cross-term has a large stabilization effect on the bowl-shaped conformer, since all adjacent torsions are neither 0° nor 180° (i.e., most of the molecule is nonplanar). However, the effect of the torsion-improper torsion term is to try to force corannulene to become more planar, and this increases the molecule's energy somewhat.

HEATS OF FORMATION

All versions of the molecular mechanics force fields (MM2, MM3) have treated heats of formation well, especially those of hydrocarbons.^{4,40} For heats of formation, MM3 calculates a root mean square (rms) error of 0.62 kcal/mol for a set of 40 alkenes and 59 conjugated hydrocarbons. The experimental rms error for this set of compounds is 0.61 kcal/mol. The introduction of the new cross-terms into MM4, while improving structures, energies, and vibrational frequencies, has also affected the heats of formation, namely the calculated energies of the molecules. The objective with MM4 is to try to maintain the overall high level of accuracy for the heats of formation already achieved by

TABLE VI.
NMR Experimental and MM3 and MM4 Calculated Energy Barriers for Corannulene-type Compounds (kcal / mol).

		Exp.	Ref.	MM3	MM4 ^a
Corannulene	bowl	0	38	0	0
	planar	11-12		14.9	11.2
Dihydrocorannulene	bowl	0	37	0	0
	planar	8.5 ± 0.5		10.0	6.7
Cyclopentacorannulene	bowl	0	39	0	0
	planar	26 ^b		32.3	25.5

^a MM4 values are ΔG^\ddagger .

^b This result is reported as a lower limit to the barrier at 127°C (ref. 39).

TABLE VII.
Semiempirical, LDF, and *Ab Initio* Calculated Energy Barriers for Corannulene-type Compounds (kcal / mol).

		AM1	LDF	HF / 3-21G	HF / 6-31G*	MP2 / 6-31G
Corannulene	bowl					
	planar	16.9 ^a	11.4 ^a	10.5 ^b	8.8 ^b	14.3 ^b
Dihydrocorannulene	bowl					
	planar	13.8 ^a	9.0 ^a	7.0 ^b	5.9 ^b	10.8 ^b

^a See ref. 37.

^b See ref. 39.

MM3 while allowing for improvements in other areas. Alkenes are included in the discussion since the heat of formation parameters for both alkenes and conjugated hydrocarbons were determined together as a set.

The unweighted MM4 rms error is 0.68 kcal/mol for 35 alkenes and 57 conjugated hydrocarbons together. Four compounds containing four-membered rings, 4-methylcyclopentene, "conjugated" ethylene,[‡] and dimethylfulvene are included in the MM3 but not the MM4 parameterization.[§]

A new weighting system was implemented for MM4. The major difference concerns the method of calculating the rms error for the heats of formation (to which the bond enthalpy increments are parameterized). With MM3 and in the alkenes work on MM4, the rms error was calculated by weighting each compound the same (although the parameters were determined by a least-squares fit in which compounds were assigned various weights), while here a weighted rms error was determined. The reason for the change here is that, while with the alkanes most of the experimental values are of good accuracy, with the conjugated hydrocarbons there are many compounds for which the accuracy is only about 2 kcal/mol but which we want to use because of their important structural differences.

When the unweighted rms errors are calculated for MM3 and MM4, the values are 0.62 and 0.68, respectively. But the weighted averages give more realistic values of 0.53 and 0.47, respectively. The heat of formation input data are given in Tables VIII–X (see Supplementary Material), and the MM4 results are in Table XI.

Methodology

Heats of formation are calculated somewhat differently for MM4 compared with the default method in MM3, although most of the calculation is similar.^{40,50} For hydrocarbons, the formation of a compound C_aH_b is expressed in eq. (4).



The standard heat of formation is by definition the difference between the enthalpies of the product

[‡] The $C_{sp^2}-C_{sp^2}$ bond in ethylene is treated as conjugated.

[§] Four-membered ring compounds will be discussed in a subsequent publication.

(C_aH_b) and reactants (graphite and hydrogen), as shown in eq. (5).

$$H_f^\circ = H_{\text{product}} - H_{\text{reactants}} \quad (5)$$

Heats of formation (H_f°) for compounds are calculated as the differences between the enthalpies of the reactants and products. MM3 calculates H_f° as in eqs. (6) and (7).

$$H_f^\circ = \text{FSE} + \text{BE} + \text{PFC} \quad (6)$$

$$\text{PFC} = \text{POP} + \text{TORS} + \text{R/T} \quad (7)$$

FSE is the steric energy of the molecule calculated by the force field (includes bonded and non-bonded interactions), BE is the normal enthalpy of increments of the molecule defined in Table XII, POP is an energy correction due to the percentage of molecules in energetically accessible higher conformational states, TORS is proportional to the number of free rotatable bonds in a molecule (excluding methyl groups), and R/T is the rotational/translational contribution plus the amount needed to convert energy to enthalpy ($4RT$).[#] The optimized MM4 values for the bond enthalpy increments involving C_{sp^2} are also given in Table XII. A complete list of the number of individual bond enthalpy increments for each compound in Table XI is given in Tables VIII and IX in the Supplementary Material.

The MM4 heat of formation calculation is carried out slightly differently than the default method used with MM3, as shown in eq. (8).^{50,51} The Supplementary Material contains the necessary input, which is outlined later.

$$H_f = \text{MH} + \text{NBE} + \text{PFC} - \text{HATOM} \quad (8)$$

$$\begin{aligned} \text{HATOM} = & -171.7 \text{ kcal/mol} \\ & \times (\text{no. of carbon atoms}) \\ & - 52.09 \text{ kcal/mol} \\ & \times (\text{no. of hydrogen atoms}) \end{aligned} \quad (9)$$

MH is the calculated molar heat content of the compound or enthalpy, which includes the final steric energy** (and the electronic energy [EE] if

[#] The $4RT$ contribution is due to the translation/rotation contribution ($6 \times 0.5RT$ for nonlinear molecules) + the correction from internal energy to enthalpy (RT).

** MH contains the final steric energy for alkenes and final energy (with electronic and sigma stretch energies) for conjugated compounds.

TABLE XI.
MM4 Calculated and Experimental Heats of Formation of Alkenes and Conjugated Hydrocarbons (kcal / mol).^a

Eqn.	Wt.	Compound	ΔH_f° Calc.	ΔH_f° Expt.	Error	Calc.- Expt.	Ref.
1	8	ethylene	12.52	12.56	0.08	-0.04	41
2	8	propene	4.99	4.88	0.16	0.11	42
3	8	<i>gauche</i> -1-butene	0.01	0.02	0.19	-0.01	41
4	6	<i>cis</i> -2-butene	-1.63	-1.67	—	0.04	43
5	6	<i>trans</i> -2-butene	-2.58	-2.67	—	0.09	43
6	8	isobutene	-4.01	-4.04	0.22	0.03	41
7	6	<i>cis</i> -2-pentene	-6.65	-6.60	0.17	-.05	41
8	6	<i>trans</i> -2-pentene	-7.58	-7.60	0.21	.02	41
9	8	2-methyl-2-butene	-10.38	-10.12	0.24	-0.26	42
10	8	2-methyl-2-pentene	-15.44	-15.96	0.35	0.52	41
11	8	2,3-dimethyl-2-butene	-17.14	-16.68	0.35	-0.46	42
12	8	2-methyl-1-butene	-8.33	-8.44	0.21	0.11	41
13	8	3,3-dimethyl-1-butene	-13.71	-14.51	0.33	0.67	42
14	8	2,3-dimethyl-1-butene	-14.45	-14.86	0.43	0.41	42
15	8	3-methyl-1-butene	-6.78	-6.61	0.16	-0.17	42
16	6	<i>tr</i> -4,4-dimethyl-2-pentene	-21.32	-21.24	0.27	-0.08	41
17	6	<i>cis</i> -4,4-dimethyl-2-pentene	-17.88	-17.37	0.34	-0.51	41
18	3	<i>trans</i> -di- <i>t</i> -butylethylene	-40.18	-39.63	—	-0.55	^b
19	3	<i>cis</i> -di- <i>t</i> -butylethylene	-29.12	-29.12	—	0.00	^b
20	6	cyclopentene	8.70	8.56	—	0.14	43
21	6	methylcyclopentene	-0.36	-0.91	0.16	0.55	41
22	6	methylenecyclopentane	2.72	2.78	0.26	-0.06	42
23	6	3-methylcyclopentene	2.04	1.76	0.16	0.28	41
24	0	4-methylcyclopentene	0.69	0.88	0.16	-0.19	57
25	6	ethylenecyclopentane	-5.05	-4.78	0.10	-0.27	44
26	6	methylcyclohexene	-10.31	-10.36	0.19	0.05	41
27	6	methylenecyclohexane	-8.03	-8.22	0.33	0.19	42
28	6	cyclohexene	-1.07	-1.20	0.17	0.13	41
29	6	cycloheptene	-2.37	-2.20	0.26	-0.17	41
30	4	norbornene	21.65	21.40	0.28	0.25	45
31	4	norbornadiene	57.29	57.37	0.36	-0.08	45
32	3	<i>trans</i> -cyclooctene	5.85	4.68	0.71	1.17	46
33	3	<i>cis</i> -cyclooctene	-5.78	-6.20	—	0.42	43
34	5	1,4-cyclohexadiene	25.73	26.30	—	-0.57	41
35	5	1,4-pentadiene	24.58	25.26	0.31	-0.68	41
36	0	barrelene	71.66	75.38	—	-3.72	47
37	0	bicyclo[2.2.2]octadiene	40.40	37.54	—	2.86	47
38	0	bicyclo[2.2.2]octene	9.05	5.96	—	3.09	47
39	0	methylene[2.2.2]octane	-2.41	-2.20	0.77	-0.21	41
40	0	methylbicyclo[2.2.2]octene	-1.85	-4.45	0.55	2.60	41
41	4	ethylene-4-norbornene	34.21	34.82	0.41	-0.61	41
42	0	ethylene ^d	14.11	12.56	0.08	1.55	41
43	10	<i>trans</i> -butadiene	25.77	26.01	0.19	-0.24	41
44	0	<i>gauche</i> -butadiene	28.74	28.08	—	0.66	^c
45	8	<i>trans</i> -isoprene	17.98	18.06	0.24	-0.08	41
46	0	<i>gauche</i> -isoprene	21.22	20.31	—	0.91	^c
47	4	2,3-dimethylbutadiene	11.38	10.79	0.26	0.59	41
48	6	<i>trans</i> -pentadiene	18.20	18.12	0.16	0.08	42
49	6	<i>cis</i> -pentadiene	18.52	19.13	0.24	-0.61	42
50	6	1,3-cyclopentadiene	32.52	32.12	0.28	0.40	41
51	6	1,3-cyclohexadiene	25.25	25.38	0.22	-0.13	41
52	6	1,3-cycloheptadiene	23.13	22.55	0.27	0.58	41

(Continues on next page)

TABLE XI.
(continued)

Eqn.	Wt.	Compound	ΔH_f° Calc.	ΔH_f° Expt.	Error	Calc.- Expt.	Ref.
53	1	1,3,5-cycloheptatriene	44.55	43.90	0.36	0.65	42
54	1	1,3,5,7-cyclooctatetraene	69.83	70.30	0.31	-0.47	41
55	0	dimethylfulvene	31.14	32.12	1.30	-0.98	41
56	10	benzene	19.88	19.81	0.14	0.07	42
57	8	toluene	12.30	12.06	0.14	0.24	41
58	8	ethylbenzene	7.22	7.15	0.22	0.07	41
59	8	<i>o</i> -xylene	4.78	4.56	0.26	0.22	41
60	8	<i>m</i> -xylene	4.13	4.14	0.18	-0.01	41
61	8	<i>p</i> -xylene	4.70	3.97	0.24	0.73	42
62	6	<i>n</i> -propylbenzene	1.83	1.89	0.19	-0.06	41
63	6	isopropylbenzene	0.67	0.96	0.25	-0.29	41
64	6	1-methyl-2-ethylbenzene	0.01	0.31	0.25	-0.30	41
65	6	1-methyl-3-ethylbenzene	-0.96	-0.43	0.27	-0.53	41
66	6	1-methyl-4-ethylbenzene	-0.39	-0.76	0.32	0.37	41
67	6	1,2,3-trimethylbenzene	-2.13	-2.26	0.29	0.13	41
68	6	1,2,4-trimethylbenzene	-2.82	-3.31	0.25	0.49	41
69	6	1,3,5-trimethylbenzene	-4.63	-3.81	0.32	-0.82	41
70	6	<i>n</i> -butylbenzene	-3.26	-3.12	0.26	-0.14	41
71	6	isobutylbenzene	-5.45	-5.14	0.31	-0.31	41
72	6	<i>s</i> -butylbenzene	-4.51	-4.15	0.29	-0.36	41
73	6	<i>t</i> -butylbenzene	-5.73	-5.40	0.29	-0.33	41
74	3	hexamethylbenzene	-21.06	-20.75	0.62	-0.31	41
75	3	tetrahydronaphthalene	4.94	6.22	0.47	-1.28	41
76	3	indane	14.29	14.16	0.43	-0.17	41
77	2	indene	38.16	39.03	0.61	-0.92	41
78	6	styrene	35.80	35.31	0.29	0.49	41
79	1	azulene	73.86	73.53	0.82	0.33	42
80	8	naphthalene	35.40	35.85	0.30	-0.45	41
81	4	biphenyl	44.60	43.53	0.60	1.07	42
82	1	acenaphthene	37.73	37.41	0.64	0.32	42
83	1	acenaphthylene	61.73	62.07	1.11	-0.34	41
84	1	9,10-dihydroanthracene	38.63	38.17	1.04	0.46	41
85	2	<i>trans</i> -stilbene	57.56	56.44	0.30	1.12	41
86	2	<i>cis</i> -stilbene	59.29	60.31	0.47	-1.02	41
87	1	1,1-diphenylethene	59.62	58.71	1.04	0.91	41
88	2	1,1-diphenylethane	33.13	33.13	0.43	0.00	41
89	2	1,2-diphenylethane	33.96	34.16	0.31	-0.20	41
90	2	anthracene	54.07	55.03	0.48	-0.96	41
91	2	phenanthracene	50.51	49.88	0.58	0.63	41
92	1	4,5-dimethylphenanthrene	44.87	46.26	1.44	-1.39	41
93	1	9,10-dimethylphenanthrene	37.51	39.93	2.02	-2.42	41
94	1	2,7-dimethylphenanthrene	34.72	34.20	0.47	0.52	41
95	1	2,2-paracyclophane	59.87	58.48	0.50	1.33	41
96	1	2,2-metaparacyclophane	52.24	52.21	0.40	0.03	41
97	0	2,2-metacyclophane	43.37	40.76	1.56	2.61	41
98	0	3,3-paracyclophane	23.33	31.00	0.51	-7.67	41
99	1	fluoranthene	69.38	69.08	0.25	0.30	41

(Continues on next page)

the molecule is conjugated) plus the vibrational energy of the molecule in the ground state (zero-point energy), and the thermal energy. NBE is the sum of the normal enthalpy of the increments of the molecule (Table XII), and HATOM is determined by eq. (9). PFC is the same term as previously described, except the POP term is calculated differently from MM3. In MM3, the POP correction

is determined from a Boltzmann distribution calculated from the final steric energies. To account for symmetry, a correction is specified which is appropriate for the point group of each conformer. However, in MM4 the Boltzmann distribution is determined directly from the conformers' free energies, which includes both steric energy and entropy considerations. The total enthalpy (MH) is

TABLE XI.
(continued)

Eqn.	Wt.	Compound	ΔH_f° Calc.	ΔH_f° Expt.	Error	Calc.- Expt.	Ref.
100	1	triphenylene	68.39	66.51	1.01	1.88	41
101	1	chrysene	67.35	66.03	1.09	1.32	41
102	1	benzo[c]phenanthrene	71.80	69.59	1.10	2.21	41
103	1	1,2-benz[a]anthracene	67.79	69.63	1.16	-1.84	41
104	0	pyrene	56.18	53.94	0.29	2.24	41
105	0	tetracene	74.23	72.30	1.25	1.93	41
106	1	5,12-dihydrotetracene	53.86	53.14	1.06	0.72	41
107	0	diphenylfulvene	93.62	96.08	3.61	-2.46	41
108	0	perylene	76.86	73.7	1.1	3.16	42
109	0	corannulene	118.76	110.8	3.6	8.00	48
110	0	coronene	77.48	61.7	—	15.78	49
111	0	tetra- <i>t</i> -butethylene	-9.34	—	—	—	—
rms					0.61	0.68	
Weighted rms						0.47	

^a Note that for the conjugated hydrocarbons, starting geometries affect the outcome of the VESCF calculation. Energies may vary slightly (usually less than 0.1 kcal/mol), especially for larger molecules, depending on the initial geometry.

^b See following discussion for 1,2-di-*t*-butylethylene.

^c The ΔH_f of the *cis*-conformer is obtained by adding the calculated MM4 *cis* / *trans* enthalpy difference to the experimental ΔH_f of the *trans*-conformer.

^d The error in the heat of formation for "conjugated" ethylene (where the $C_{sp^2}-C_{sp^2}$ bond is treated as conjugated by the program) is considerably larger than the experimental one. The $C=Cl$ bond increment in MM4 is an optimizable parameter, whereas in MM3 it was fixed as the MM3 calculated value of the electronic energy for conjugated ethylene (-129.37 kcal/mol). Thus treating molecules with ethylene-type bonds as conjugated will lead to significant errors. This error is also present in MM3 but has been averaged out between the "unconjugated" and "conjugated" ethylenes.

TABLE XII.
Normal Enthalpy Increments for Alkenes / Conjugated Hydrocarbons.

Increment	Best Value	Explanation
* c—h	-105.7262	$C_{sp^3}-H$ type bond
* c—c	-89.1945	$C_{sp^3}-C_{sp^3}$ type bond
C—C	-90.1872	$C_{sp^2}-C_{sp^3}$ type bond
* me	-0.0964	methyl group attached to C_{sp^3}
ME ^a	-0.0364	methyl group attached to C_{sp^2}
* iso	-1.2575	two methyl groups attached to C_{sp^3}
ISO1	-1.2207	two methyl groups attached to C_{sp^2}
SEC1 ^b	-0.8945	secondary group attached to C_{sp^2}
tBUT	-1.9612	quaternary group attached to C_{sp^2}
C=Cl	-131.0967	$C_{sp^2}-C_{sp^2}$ type bond (not involved in conjugation)
C=Cd	-21.1478	$C_{sp^2}-C_{sp^2}$ type bond (involved in conjugation)
ISOd	8.8874	an C_{sp^2} and an C_{sp^3} attached to C_{sp^2}
SECd ^b	9.6073	two C_{sp^2} 's attached to C_{sp^2}
TERd ^a	22.0828	three C_{sp^2} 's attached to C_{sp^2}
* r5	4.4694	5-membered ring
* r6	4.9446	6-membered or larger ring
* TORS	0.5715	number of free rotatable bonds

* These heat parameters already were determined from heats of formation data for alkanes.

^a This parameter appears only in MM4.

^b SECI and SECd appear as one term "SEC" in MM3.

then calculated from the percentage of each conformer multiplied by its enthalpy. The MM4 POP term is the difference between this total enthalpy and the enthalpy of the conformer with the lowest energy.

MM4, unlike MM3, includes the vibrational energies of the molecules. Instead of assuming that the vibrational energies will average out in the data set and are implicit in the BE terms, they are explicitly included. As previously mentioned, this is especially important for calculating barriers, where the energy difference between the bottoms of the wells and first vibrational levels for two conformations can be significant.

trans- and *cis*-Di-*t*-butylethylene

The heats of formation of *trans*- and *cis*-di-*t*-butylethylene have not been determined directly by experiment. They were derived for MM3 and MM4 by the following method, which is diagrammed in Figure 3.⁵² First, the heat of formation for 2,2,5,5-tetramethylhexane was calculated using MM3/MM4. Next, the heats of hydrogenation of the *trans*- and *cis*-isomers were added to the calculated heat of formation of 2,2,5,5-tetramethylhexane to give the ΔH_f for *trans*-/*cis*-di-*t*-butylethylene.

Two different experiments report heats of hydrogenation for *trans*-/*cis*-di-*t*-butylethylene.^{53,54} The MM3 calculated heats of formation were determined from the Turner/Nettleton/Perelman (TNP) study, which reported heats of hydrogenation determined in acetic acid.⁵³ A correction was made to the *cis* compound. Heats of solution for alkanes have been found to be more positive than those of their corresponding *cis*-alkenes by about 0.6 kcal/mol relative to their gas phase values.⁵⁵ This difference has been attributed to an exothermic alkene-solvent molecule pair formation, which occurs in acetic acid for molecules with strong dipole moments and/or hydrogen bonding.⁵⁶ This has been found to occur in the *cis* (but not the *trans*) compound, presumably because the *cis*-conformer has a dipole moment and forms a

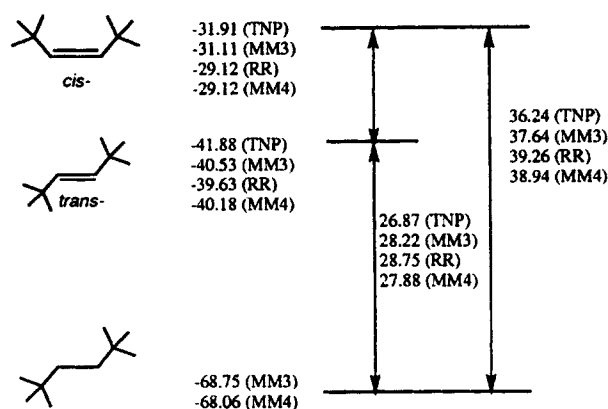


FIGURE 3. Heats of formation of *trans*- and *cis*-di-*t*-butylethylene (kcal/mol).

stronger hydrogen bond. Thus the quantity 0.6 kcal/mol is added to the MM3 "experimental" *cis* heat of formation value.

The second study by Rockenfeller and Rossini (RR) reported heats of hydrogenation determined in the pure liquid, and no correction was needed.⁵⁴ Extensive studies by Rogers have shown that heats of hydrogenation of alkenes in alkane solvent are very close to those measured in the gas phase. Thus, the RR heat of hydrogenation data were chosen for calculating the MM4 "experimental" ΔH_f 's for *trans*- and *cis*-di-*t*-butylethylene from the MM4 ΔH_f for 2,2,5,5-tetramethylhexane.

Both TNP and RR report heats of hydrogenation (H_h) data not only for *trans*- and *cis*-di-*t*-butylethylene but also for *trans*- and *cis*-4,4-dimethyl-2-pentene. The heats of hydrogenation and heats of formation results are reported in Table XIII. Data from vapor pressure/temperature measurements were used to determine ΔH_f 's for *trans*-/*cis*-4,4-dimethyl-2-pentene of -21.22 and -17.36 kcal/mol,⁴¹ which are much closer to the RR results.⁵⁴

4-Methylcyclopentene

An experimental value of 2.06 kcal/mol is given in the MM3 heats of formation set for 4-methyl-

TABLE XIII.
 ΔH_h 's and ΔH_f 's for *trans*-/*cis*-4,4-Dimethyl-2-Pentene (kcal/mol).

	TNP		RR	
	ΔH_h	ΔH_f^a	ΔH_h	ΔH_f^a
4,4-dimethyl- <i>trans</i> -2-pentene	-26.51	-22.69	-27.74	-21.46
4,4-dimethyl- <i>cis</i> -2-pentene	-30.80	-18.40	-31.66	-17.54

^a Calculated using ΔH_f of -49.20 kcal/mol for 2,2-dimethyl-2-pentane (see ref. 42).

cyclopentene.⁴ Although this compound is referenced to Cox and Pilcher, the ΔH_f value given in this reference is 3.50 ± 0.5 kcal/mol.⁴² A later thermodynamic study found the ΔH_f (at 465 K) for 4-methylcyclopentene to be 0.88 kcal/mol.⁵⁷ This value was obtained by measuring the enthalpies of isomerization for methylcyclopentenenes from 298 to 633 K. The MM3 calculated ΔH_f is 2.19 kcal/mol. A study by Schmitz and Chen, which parameterized alkenes to HF/6-31G* *ab initio* energies, calculated an ΔH_f of 1.36 kcal/mol.⁵⁸ The MM4 ΔH_f result is 0.69 kcal/mol. This compound is not weighted in the parameterization set since it is not clear which experimental value is best.

The Bicyclooctene Series

Unfortunately, few experimental data are available for the strained bicyclooctene series (see Fig. 4). Thus, *ab initio* Hartree-Fock (HF) calculations at the 6-31G*//3-21G level of theory were carried out,⁴⁷ and heats of formation were determined using the atom equivalent method of Ibrahim and Schleyer.⁵⁹ Neither MM3 nor MM4 reproduce these calculated heats of formation well. A group equivalent scheme for calculating heats of formation using HF/6-31G* calculations⁶⁰ has now been extended to alkenes, including barrelene, bicyclo[2.2.2]octadiene, and bicyclo[2.2.2]octene, by Schmitz and Chen.⁵⁸ All of the results are summarized in Table XIV.

Both *ab initio* calculated heats of formation for barrelene are greater than the MM3 and MM4 values, especially than the MM4 one. The fact that barrelene is antiaromatic may explain partly why the MM4 heat of formation is calculated too low. The unfavorable pi-orbital overlap should increase the energy of barrelene. However, MM4 does allow resonance between nonbonded atoms, but with the neglect of overlap approximation for the pi-system. The destabilization energy that would re-

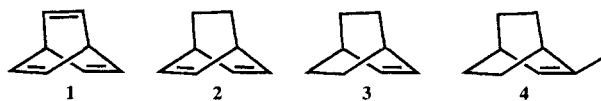


FIGURE 4. Olefinic compounds in the bicyclooctene series.

sult from this overlap is thus not taken into account in the heat of formation. In other words, any energy due to the unfavorable electronic interaction between the double bonds (antiaromaticity) is not included in the overall MM4 calculated energy of barrelene.⁴⁷ (The heat of formation of barrelene calculated by treating the molecule as conjugated is about 76.5 kcal/mol, but this is a result of the error that such a calculation makes for an isolated double bond [ethylene, Table XI] times 3.) Also, barrelene has many torsions involving atom types 2-1-2-2 and 2-1-2-112. Small changes in these torsional parameters could have significant effects on the calculated steric energy of barrelene.

The remaining MM4 values for compounds in the bicyclooctene series are all calculated to be more positive than the *ab initio* results, although they are closer to the ones from the group equivalent scheme of Schmitz and Chen.⁵⁸ The MM4 results are also 3–4 kcal/mol higher than available experimental results for bicyclo[2.2.2]octene and methylbicyclo[2.2.2]octene. The 1-1-2-2 and 1-1-2-112 torsions are involved in these compounds. Trying to reproduce the *ab initio* results for the bicyclooctene series would lead to significant deviations of different MM4 results from their corresponding experimental values, including heats of formation of compounds which contain these parameters. We have to conclude that we do not understand the heats of formation of this series of compounds, and we do not recommend that the MM3 or MM4 values be relied on.

TABLE XIV.
Summary of Heats of Formation for the Bicyclooctene Series.

		Expt.	MM3	MM4
1	Barrelene	75.38 ^a / 78.84 ^b	73.97	71.66
2	Bicyclo[2.2.2]octadiene	37.54 ^a / 39.50 ^b	38.93	40.40
3	Bicyclo[2.2.2]octene	5.96 ^a / 6.46 ^b / 4.90 ^c	7.22	9.05
4	Methylbicyclo[2.2.2]octene	– 4.45 ^c	– 1.16	– 1.85

^a Determined by *ab initio* methods using an atom equivalent method as described in ref. 47.

^b Determined by *ab initio* methods using a group equivalent method as described in ref. 58.

^c Experimentally determined, gas phase; see ref. 41.

Errors for Conjugated Compounds

The biggest errors in the MM4 heats of formation occur (apart from the bicyclooctene series) for the nonplanar conjugated compounds such as biphenyl and *cis*- and *trans*-stilbene and for the larger-sized planar conjugated compounds. Whether the deviations result from problems with the electronic energies from the VESCF calculation, sigma energy approximations, or torsional parameters remains unclear. As mentioned in the previous article,² the torsion-torsion cross-term plays a large role in stabilizing energies of more highly aromatic compounds, especially those with aromatic six-membered rings with nearly equal bond orders. The greater the difference in the bond orders of adjacent bonds, the less stabilization is contributed by the torsion-torsion cross-term. (For a weakly conjugated system, one bond order is close to 1, so the value of E_{π} is close to 0.) This term seems to be more critical for stabilizing larger multi-ring systems, where small errors in electronic energy per ring can quickly add up, resulting in positive heat of formation errors.

Strain Energies

The sigma strain energy of a molecule is determined from the difference between the heat of formation of the molecule in question and that of its hypothetical strainless analog; the inherent strain energy is equal to the sigma strain minus the POP and TORS contributions. The twelve com-

pounds in Table XV were used to obtain strainless heats of formation parameters, which were determined in the same manner as the regular ones, except that the MM4 values were used for the experimental heats of formation and the enthalpies and POP and TORS terms were set to zero. The strainless heat parameters are given in Table XVI. Inherent strain energies for some alkenes and conjugated hydrocarbons are given in Table XVII. The bond enthalpy increments and necessary input for the compounds in Table XV are listed in Tables XVIII-XX in the Supplementary Material. An examination of Table XVII shows that the strain energies are easily understood in terms of standard principles of physical organic chemistry.⁶¹

Resonance Energies

As in MM3, the MM4 resonance energies are considered to have sigma (σ) and pi (π) components.⁴ For planar systems, these quantities are separable. However, for nonplanar ones, the distinction is undefined. Both MM3 and MM4 determine the sigma strain energy as a measurement of the total strain energy, which was discussed earlier. The pi-resonance energy calculation is presented next, and it is only carried out on planar pi-systems. A more complete discussion has been given concerning these problems and the MM method of calculating resonance energies.⁴

The MM definition for pi-resonance energy is basically the same as Dewar's.⁶² MM4 resonance

TABLE XV.
MM4 Calculated Strainless Heats of Formation of Alkenes and Conjugated Hydrocarbons (kcal / mol).

Eq.	Wt.	Compound	H_f° (Calc.)	H_f° (MM4)	Calc - MM4
1	1	Ethylene	12.53	12.52	0.01
2	1	Propene	4.98	4.99	-0.01
3	1	<i>trans</i> -2-Butene	-2.57	-2.58	0.01
4	1	Isobutene	-4.01	-4.01	0.00
5	1	<i>trans</i> -2-Pentene	-8.22	-8.22	0.00
6	1	3,3-Dimethyl-1-butene	-14.28	-14.28	0.00
7	1	3-Methyl-1-butene	-7.56	-7.56	0.00
8	1	<i>trans</i> -Butadiene	25.91	25.91	0.00
9	1	Benzene	19.88	19.88	0.00
10	1	Toluene	12.29	12.29	-0.01
11	1	<i>para</i> -Xylene	4.70	4.70	0.00
12	0	Styrene	32.37	35.80	-3.43
13	0	Cyclopentadiene	27.34	32.52	-5.18
14	1	Naphthalene	35.40	35.40	0.00
rms					0.0037

TABLE XVI.
Strainless Bond Enthalpy Increments for Alkenes / Conjugated Hydrocarbons.

Increment	Best Value	Explanation
* C—H	−98.4375	C _{sp} ³ —H type bond
* C—C	−84.8479	C _{sp} ³ —C _{sp} ³ type bond
C—C	−86.5503	C _{sp} ² —C _{sp} ³ type bond
* me	0.1915	methyl group attached to C _{sp} ³
ME ^a	−0.0047	methyl group attached to C _{sp} ²
ISOI	−1.4367	two methyl groups attached to C _{sp} ²
SECI ^b	−1.2386	secondary group attached to C _{sp} ²
tBUT	−2.3071	quaternary group attached to C _{sp} ²
C=Cl	−131.4771	C _{sp} ² —C _{sp} ² type bond (not involved in conjugation)
C=Cd	−14.0063	C _{sp} ² —C _{sp} ² type bond (involved in conjugation)
ISOd	6.7169	an C _{sp} ² and an C _{sp} ³ attached to C _{sp} ²
SECD ^b	6.7469	two C _{sp} ² 's attached to C _{sp} ²
TERd ^a	14.1773	three C _{sp} ² 's attached to C _{sp} ²
* r6 ^c	4.9446	6-membered or larger ring

* These heat parameters already were determined from strainless heats of formation data for alkanes.

^a This parameter appears only in MM4.

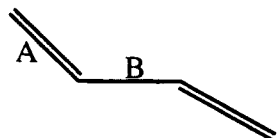
^b SECI and SECD appear as one term "SEC" in MM3.

^c The r6 term also applies for 5-membered rings; their regular heat parameters are very similar anyway, and since 5-membered rings are strained, it would be difficult to determine an independent parameter.

TABLE XVII.
MM4 Inherent Strain Energies of Alkenes and Conjugated Hydrocarbons (kcal / mol).

Compound	Inherent Strain Energy	Compound	Inherent Strain Energy
1-Butene	+0.04	Cyclohexene	−0.18
trans-2-Pentene	+0.00	Norbornene	+18.64
cis-2-Pentene	+1.00	2,3-Dimethylbutadiene	−0.53
2-Methyl-2-Butene	+1.18	Cyclopentadiene	+0.23
trans-4,4-dime-2-pentene	−0.06	Cyclooctatetraene	+16.50
cis-4,4-dime-2-pentene	+3.38	n-Propylbenzene	−0.12
transDi-t-butylethylene	−0.24	Hexamethylbenzene	+4.54
cis-Di-t-butylethylene	+10.82	Styrene	+2.86
Cyclopentene	+3.74		

energy parameters are determined for double (A) and single (B) bond components of the kekule forms of conjugated molecules, as illustrated in Figure 5. Linear transoid polyenes by definition are strainless and have zero resonance energy.⁶² Thus, in order to determine resonance energy parameters, ethylene, *trans*-butadiene, *trans*-

**FIGURE 5.** Kekule bond components.

hexatriene, and *trans*-octatetraene were fit by eq. (10). A least-squares fitting was used to determine the resonance energy parameters (E_A and E_B). N_A and N_B (in general) are the number of double and single bonds in the most stable kekule form, respectively. EE is the electronic energy calculated by the VESCF method.

$$N_A E_A + N_B E_B - EE = 0 \quad (10)$$

As can be seen in Table XXI, the aforementioned four molecules have resonance energies which deviate very slightly from zero. E_A and E_B were determined to be −129.2419 and −95.8850, respectively, for MM4.

TABLE XXI.
Input Used to Determine Resonance Energy
Parameters and Actual Calculated Energies
(kcal/mol) for Four Linear Polyenes.

	N _A	N _B	EE	Theoretical Resonance E	Calculated Resonance E
ethylene	1	0	-129.37	0.00	0.12
<i>trans</i> -butadiene	2	1	-354.21	0.00	-0.15
hexatriene	3	2	-579.43	0.00	-0.06
octatetraene	4	3	-804.69	0.00	0.09

Resonance energies for some compounds were calculated from the resonance energy parameters and are shown in Table XXII. Benzene has a resonance energy of 18.1 kcal/mol in this calculation, similar to the Dewar value (20.0 kcal/mol).⁶² Fused benzenoid systems show familiar trends. Note that the resonance energy of azulene is negligible (-0.3 kcal/mol) and cyclodecapentaene is small (5.9 kcal/mol) compared to benzene.

ENTROPIES AND HEAT CAPACITIES

Classical methods employing principles of statistical mechanics can be used to determine thermodynamic quantities of interest. MM3 and MM4 calculate entropies and heat capacities as the sum of the translational, rotational, and vibrational contributions to the partition function.⁶³ Classical equations have been derived for these components.⁶³ Thus, entropies at a given temperature can be determined if the mass (translational), moments of inertia and symmetry number (rotational), and vibrational levels (vibrational) for a given molecule

can be calculated. Note that the block-diagonal Newton-Raphson optimizer in MM2 cannot compute the second derivatives needed to determine the force constant matrix (and hence vibrational frequencies). However, the implementation of the full-matrix optimization scheme allows MM3 and MM4 to calculate the vibrational levels (the harmonic approximation is assumed). For molecules with multiple minima, the percentage of each conformer needs to be determined from the free energies of the conformers in order to calculate the total entropy [see eq. (11)]. The entropy of mixing is also included for molecules which have multiple minima, as shown in eq. (12), where x_a is the mole fraction of conformer a.

$$\Delta S_{\text{total}}^{\circ} = \sum_a x_a \Delta S_a^{\circ} + \Delta S_{\text{mix}}^{\circ} \quad (11)$$

$$\Delta S_{\text{mix}}^{\circ} = -R \sum_a x_a \ln x_a \quad (12)$$

Both MM3 and MM4 will calculate for any conformation all of these things at any desired temperature (except the items involving mixing, which of course are not properties of a single conformation). Entropies are presented for completeness in Tables XXIII-XXV. As in MM3, this information was not used in the parameterization process but is an independent check on the accuracy of the results. The entropies calculated in this way are given in Table XXIII for alkenes (preliminary). Some systematic negative errors are seen for the MM4 results for alkenes.

For MM4, a TORS correction of 0.40 eu is added to the entropies of molecules which have low rotational barriers (< 5 kcal/mol) involving heavy atoms. It has been found for alkanes that this correction is necessary to calculate entropies for

TABLE XXII.
Resonance Energies (kcal/mol) of Planar Conjugated Compounds.

Compound	Resonance Energy	Compound	Resonance Energy
Ethylene	0.1	Anthracene	32.8
<i>trans</i> -1,3-Butadiene	-0.2	Phenanthrene	39.4
<i>trans</i> -1,3,5-Hexatriene	-0.1	Pyrene	43.0
<i>trans</i> -1,3,5,7-Octatetraene	0.1	Tetracene	36.8
Benzene	18.1	1,2-Benzanthracene	46.5
1,3,5,7-Cyclooctatetraene	-3.4	Chrysene	50.0
Cyclodecapentaene	5.9	Triphenylene	53.1
Naphthalene	27.2	Kekulene ^a	121.1
Azulene	-0.3	Biphenyl (planar)	34.3

^a Kekulene (ref. 4) was calculated to have one negative eigenvalue in its force constant matrix by MM4.

TABLE XXIII.
Preliminary Entropies (S° , cal / mol · deg or eu) of Alkenes at 298 K.

	Exp. ^a	Initial MM4	ΔS_{mix} MM4	Final MM4	Error	MM3	Error
Ethylene	52.45	52.44	—	52.44	−0.01	52.34	−0.11
Propene	63.80	63.41	—	63.41	−0.39	63.51	−0.29
1-Butene	73.04	72.38	0.55	72.93	−0.11	73.07	+0.03
cis-2-Butene	71.90	71.08	—	71.08	−0.82	71.32	−0.58
trans-2-Butene	70.86	70.09	—	70.09	−0.77	70.45	−0.41
Isobutene	70.17	69.51	—	69.51	−0.66	69.99	−0.18
2,3-Dimethyl-2- Butene	87.15	86.55	—	86.55	−0.60	87.60	+0.45
Cyclopentene	69.23	69.60	—	69.60	+0.37	69.60	+0.37
Cyclohexene	74.27	73.88	—	73.88	−0.39	74.00	−0.27
1,4-Pentadiene	79.70	77.58	1.79	79.37	−0.33	79.48	−0.22
2-Methyl-1-butene ^b	81.73	79.92	0.89	80.81	−0.92	80.52	−1.21
1-Pentene ^b	83.08	80.04	2.39	82.43	−0.65	82.37	−0.71
trans-2-Pentene ^b	81.81	80.45	0.52	80.97	−0.84	81.49	−0.32
rms					0.59^c		0.50
ave.					−0.37^c		−0.26

^a See ref. 64 unless otherwise noted.^b See ref. 65.^c Before corrections.**TABLE XXIV.**
Entropies (S° , cal / mol · deg) of Alkenes with TORS and ME Corrections.

	Exp. ^a	MM4	Δ	TORS	w/ TORS	Δ	ME	w/ ME	Δ
Ethylene	52.45	52.44	−0.01	0	52.44	−0.01	0	52.44	−0.01
Propene	63.80	63.41	−0.39	0	63.41	−0.39	1	63.66	−0.14
1-Butene	73.04	72.93	−0.11	1	73.33	+0.29	0	73.55	+0.29
cis-2-Butene	71.90	71.08	−0.82	0	71.08	−0.82	2	71.58	−0.32
trans-2- Butene	70.86	70.09	−0.77	0	70.09	−0.77	2	70.59	−0.27
Isobutene	70.17	69.51	−0.66	0	69.51	−0.66	2	70.02	−0.16
2,3-Dimethyl- 2-Butene	87.15	86.55	−0.60	0	86.55	−0.60	4	87.56	+0.40
Cyclopentene	69.23	69.60	+0.37	1	70.00	+0.77	0	70.04	+0.77
Cyclohexene	74.27	73.88	−0.39	0	73.87	−0.39	0	73.87	−0.39
1,4- Pentadiene	79.70	79.37	−0.33	2	80.17	+0.47	0	80.17	+0.47
2-Methyl-1- butene ^b	81.73	80.81	−0.92	1	81.21	−0.52	1	81.46	−0.27
1-Pentene ^b	83.08	82.43	−0.65	2	83.23	+0.15	0	83.23	+0.15
trans-2- Pentene ^b	81.81	80.97	−0.84	1	81.37	−0.44	1	81.62	−0.19
rms			0.57			0.52			0.35
ave.			−0.37			−0.14			−0.05

^a See ref. 64 unless otherwise noted.^b See ref. 65.

TABLE XXV.
Entropies (S° , cal / mol · deg) Conjugated Hydrocarbons at 298 K.

	Exp. ^a	Initial MM4	ΔS_{mix} MM4	TORS	Final MM4	Δ	MM3	Δ
1,3-Butadiene	66.6	66.99	0.85	—	67.84	+1.2	66.5	−0.1
Benzene	64.3	64.64	—	—	64.64	+0.4	65.1	+0.8
Toluene ^b	76.6	78.20	—	—	78.20	+1.6	78.5	+1.9
Styrene	82.5	83.01	—	0.40	83.41	+0.9	81.3	−1.2
Naphthalene	80.2	80.19	—	—	80.19	0.0	81.1	+0.9
Cyclooctatetraene	78.1	78.40	—	—	78.40	+0.3	77.9	−0.3
Biphenyl	93.9	93.36	—	0.40	93.76	−0.1	94.8	+0.9
rms						0.85		1.0
ave.						+0.61		+0.41

^a See ref. 64.^b Toluene has one low vibrational frequency ($10 < \nu < 40 \text{ cm}^{-1}$). See discussion concerning free internal rotation and Table XXVIII.

compounds which have these low rotational barriers. The harmonic approximation for these torsional potentials results in more widely spaced energy levels than actually exist. Thus, these states are calculated to be less available, and the thermodynamic quantities (enthalpy, entropy) for the aforementioned compounds would be calculated too low. A TORS correction is already incorporated into the heats of formation calculation by both MM3 and MM4 for this reason, as mentioned earlier.

Another systematic error seems to occur for compounds with a methyl group attached to an C_{sp^2} atom. The addition of 0.25 eu for each such methyl group also improves the entropy values and is attributed to the same physical effect. The fundamental frequencies should be higher for methyl than for the heavy atom case, and the levels therefore more widely spaced, so the numerical value of the term is smaller (no such value is used in alkanes, where the barriers are higher than in the alkenes and the values needed would be smaller). Table XXIV gives a summary of the entropies of the alkenes with and without the TORS and ME increments and the resulting corrections all included. Note that the systematic errors are eliminated by using these terms (average error −0.37 eu without, −0.05 eu with), and the rms error is much reduced (0.57 and 0.35 eu, respectively).

Entropies for conjugated hydrocarbons are presented in Table XXV. MM4 calculates the minimum energy structure for styrene to be slightly twisted about the formally single bond. Thus, an entropy of mixing term ($-R \ln 2 = 1.4 \text{ eu}$) is added by the program to the computed entropy.

This should not occur, however, as the barrier to the cis structure is negligible (0.01 kcal/mol) and is well below the first vibrational level. Thus, when the zero-point vibration is taken into account, styrene really exists as a planar (cis) form, and the MM4 entropy is 83.0 eu (not the 84.4 eu reported by the program), excluding the TORS contribution. A TORS term should be included for styrene and biphenyl if the same criterion is used for conjugated hydrocarbons as for alkenes. Although this correction adjusts biphenyl closer to its experimental value, styrene is already calculated 0.5 eu larger than experiment, and the TORS raises the entropy an additional 0.40 eu. The experimental value for styrene may be questionable because it polymerizes, which could make it difficult to measure accurately its entropy and heat capacity experimentally.

The heat capacity can be determined by differentiating the enthalpy with respect to temperature. Classically, this can be simplified by including contributions from the external energy (R), the translational part ($1.5R$), and for nonlinear molecules, the rotational part ($1.5R$), where the gas constant $R = 1.987 \text{ cal/mol} \cdot \text{deg}$. The vibrational part is the sum of terms due to the different normal vibrations, as for the entropy.⁶³ This quantity is much more dependent on the vibrational part of the calculation than is the entropy. Consequently, due largely to the errors from the harmonic approximation, the heat capacities are more likely to be calculated in error of experiment by MM3 and MM4. Heat capacities for alkenes and conjugated hydrocarbons are presented in Tables XXVI and XXVII, respectively.

For cyclopentene, the calculated MM4 heat ca-

TABLE XXVI.
Heat Capacities (C_p° , cal / mol · K) of Alkenes at 298 K.

	Exp. ^a	MM4	Error	MM3	Error
Ethylene	10.41	10.24	-0.17	10.08	-0.33
Propene	15.27	15.09	-0.18	15.16	-0.11
1-Butene	20.47	19.98	-0.49	20.12	-0.35
cis-2-Butene	18.86	20.24	+1.38	20.44	-1.58
trans-2-Butene	20.99	20.44	-0.55	20.64	-0.35
Isobutene	21.30	20.60	-0.70	20.87	-0.43
2,3-Dimethyl-2-Butene	29.54	31.97	+2.43	32.45	+2.91
Cyclopentene	17.95	20.06	+2.11	20.09	+2.14
Cyclohexene	25.10	23.98	-1.12	24.10	-1.00
1,4-Pentadiene	25.10	22.87	-2.23	24.03	-1.07
rms			1.40		1.36
ave.			+0.05		-0.02

^a See ref. 64.

capacity (and entropy) results in large positive errors from experiment. The heat capacity error must be due to an error in the vibrational frequency calculations if experiment is correct. However, MM4 calculates the lowest frequency of cyclopentene to be 183 cm^{-1} , which is much higher than the corresponding experimental IR frequency (127 cm^{-1}).⁶⁶ Thus, either the heat capacity experiment or the IR frequency is probably in error.

Corrections for Free Internal Rotation

Another difficulty arises for toluene, which has a low vibrational frequency ($< 40\text{ cm}^{-1}$). Low vibrational frequencies result in significant deviations from the harmonic approximation for the vibrational potential well, which can result in inaccurately calculated entropies. The MM3 and MM4

programs give a warning message when one or more of the vibrational frequencies are less than 40 cm^{-1} . For this situation, one half of the entropy due to the low frequency is added, and the error of the approximation is taken to be 100% of the quantity added. This gives a result that is more in line with experiment, with very conservative error limits. Toluene has an almost free methyl rotor, whose frequency is calculated by MM4 to be 12 cm^{-1} . The entropy and heat capacity contributions from this frequency are calculated by MM4 to be 7.729 eu and 1.985 cal/mol · K, respectively. Applying the aforementioned treatment gives the entropy and heat capacity values in the first row of Table XXVIII. Note that the uncertainty in the entropy here is large (3.9 eu), but the calculated value is off by 2.5 eu, well within the uncertainty.

The standard corrections for entropy and heat

TABLE XXVII.
Heat Capacities (C_p° , cal / mol · K) of Conjugated Hydrocarbons at 298 K.

	Exp. ^a	MM4	Error	MM3	Error
1,3-Butadiene	19.01	18.14	-0.87	18.70	-0.31
Benzene	19.52	19.92	+0.40	20.38	+0.86
Toluene ^a	24.77	25.22	+0.45	25.65	+0.88
Styrene	29.18	28.86	-0.32	29.25	+0.07
Naphthalene	31.68	31.88	+0.20	32.62	+0.94
Cyclooctatetraene	29.16	28.66	-0.50	29.80	+0.64
Biphenyl	38.80	39.61	+0.81	40.55	+1.75
rms			0.56		0.93
ave.			+0.02		0.69

^a See ref. 64.^b Toluene has one low vibrational frequency ($10 < \nu < 40\text{ cm}^{-1}$). See discussion concerning free internal rotation.

TABLE XXVIII.
Two Methods of Correcting S° and C_p° for Toluene.

	S° (cal / mol · K)			C_p° (cal / mol · K)		
	MM4 Uncorr.	W / Corr.	Δ	MM4 Uncorr.	W / Corr.	Δ
1	75.26	79.12 ± 3.9	+2.5	24.23	25.22 ± 0.99	+0.45
2	75.26	78.20	+1.6	24.23	25.22	+0.45

capacity are given by Herzberg for free internal rotation (fir) of one methyl group against the rest of a relatively heavier frame, as shown in eqs. (13) and (14).⁶³

$$S_{\text{fir}}^\circ = 2.2868 \log_{10} T - 2.714 \quad (13)$$

$$C_{p \text{ fir}}^\circ = 1.5R \quad (14)$$

Applying these corrections to toluene at $T = 298$ K gives a contribution of 2.94 eu for the entropy and 0.99 cal/mol · degree for the heat capacity. These corrections are given in the second row in Table XXVIII. This entropy correction gives a value somewhat closer to, but still larger than, experiment.

VAN DER WAALS INTERACTIONS

As mentioned in the previous article,² the van der Waals parameters for hydrogens attached to alkane and olefinic carbons are now different for MM4: The alkane hydrogen is still type 5, as in MM3, and the alkene type hydrogen is now type 112 in MM4. It seems logical that hydrogen atom types for each respective carbon should be treated individually, since the individual C_{sp^3} - and C_{sp^2} -type carbon atom types are treated this way. Again,

in most cases, the same parameters could have been used for hydrogens attached to either carbon type, but this would have led to some problems with crystal structures and the spectra of conjugated molecules, namely the C—H stretching frequencies of *in*-cyclophanes.

An *in*-cyclophane consists of an aromatic six-membered ring with alternate branching sidechains which join to a common carbon, whose methine hydrogen points toward the center of the ring. The following compounds are displayed in Figure 6: *in*-[3^{4,10}][7]metacyclophane (2.1a), 2,6,15-trithia[3^{4,10}][7]metacyclophane (2.1b), 2,7,16-trithia[3^{5,11}][8]metacyclophane (2.1c), 2,8,17-trithia[3^{5,12}][9]metacyclophane (2.1d), and 2,8,17-trithia-*in*-[4^{5,12}][9]metacyclophane (2.1e).⁷⁰

In MM3, a hydrogen attached to either a C_{sp^3} - or C_{sp^2} -type carbon is assigned the same atom type (type 5). Although hexamethylbenzene,⁶⁷ benzene,⁶⁸ and biphenyl⁶⁹ crystal packing data are fit well, the *in*-cyclophane C—H stretching frequencies were calculated 57–95 cm⁻¹ too high (see Table XXIXa). Lowering them was accomplished in part by reducing the cubic-stretch term for C—H bonds, which was done to fit alkane C—H stretching frequencies better. The cubic-stretch term is 2.55 for all bonds in MM3, but the MM4

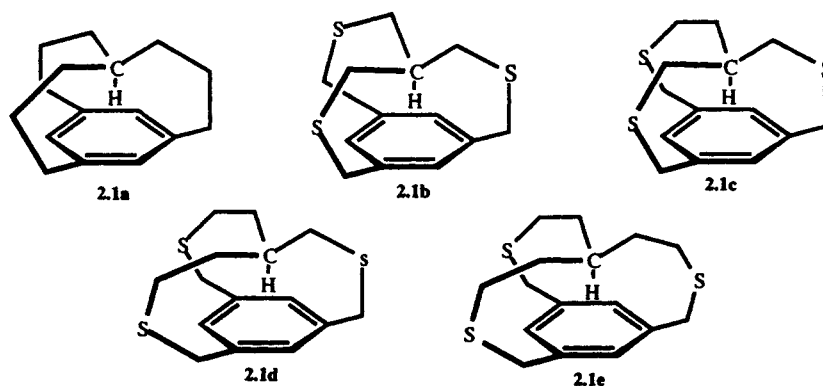


FIGURE 6. Structures of five *in*-cyclophanes.

TABLE XXIXa.
***In-cyclophane Stretching Frequencies (cm⁻¹).*^a**

Compd.	IR C—H ν	MM3	Δ	MM4	Δ
2.1a	3325	3415	+90	3306	-19
2.1b	3260	3338	+78	3242 ^b	-18
2.1c	3147	3217	+70	3141 ^b	-6
2.1d	< 3100	3143	> 43	3067 ^b	—
2.1e	< 3100	3116	> 16	3054 ^b	—

^a See ref. 70. Some of the improvements for compounds 2.1b–e resulted from the inclusion of the torsion-bend term for angles containing sulfur.

^b These frequencies are slightly dependent on sulfur parameters not yet finalized, and are subject to minor revision.

value is lowered to 2.20 for all bonds to H (or deuterium) and raised to 3.00 for all other bonds. To reduce the *in-cyclophane* C—H stretching frequencies further, the C...H van der Waals radius for a C_{sp²}...H (type 2...5) interaction could be decreased; however, this change would reduce the benzene crystal packing volume, which is already calculated slightly lower than the experimental value. Since the *in-cyclophane* C—H stretching frequency involves a hydrogen attached to a C_{sp³}-type carbon, if a different atom type is assigned to the hydrogen attached to a C_{sp²}-type carbon, both the benzene crystal and *in-cyclophane* C—H stretching frequencies can be fit simultaneously. Thus, a hydrogen attached to a C_{sp³}-type carbon will remain atom type 5, while a hydrogen attached to a C_{sp²}-type carbon will be assigned atom type 112 (see Table XXIXb).

Lowering the van der Waals radius of an atom reduces the minimum energy distance between two nuclei, allowing them to approach closer to each other and thereby shifting the minimum of the potential well. Thus, a major effect of decreasing the 2...5 and 2...112 van der Waals radius parameters is to reduce the MM4 crystal packing volume for hexamethylbenzene and benzene, respectively. In the case of *in-cyclophanes*, lowering the 2...5 van der Waals radius parameter allows

the methine H to come closer to the ring and lowers the C—H stretching frequencies for the compounds in Figure 6 and Table XXIXa, which improves the agreement between an experimental H...ring distance (2.1e) and infrared C—H frequencies (2.1a–e). To a lesser extent, this change will also decrease the calculated heat of sublimation for the hexamethylbenzene crystal (see Table XXX).

The structure of compound 2.1b has been determined by X-ray diffraction at room temperature ($R = 0.026$).⁷⁰ An interesting feature of this molecule is the relatively short H...ring distance. Reducing the 2...5 van der Waals radius lowers this distance for MM4 relative to MM3, and it is now much closer to experiment (see Table XXXI and Fig. 7). MM4 also shows improvement over MM3 for the S—C₄—C₅ and C₁—C₃—S angles, although this is partially due to the inclusion of the torsion-bend term for this angle type.⁷²

Raising the value of epsilon increases the depth of the potential well, which will hinder the close approach of two atoms towards each other. This will increase the calculated heat of sublimation for hexamethylbenzene. For the *in-cyclophanes*, raising the value of epsilon will also increase the H...ring distance as well as the C—H stretching frequencies.

The crystal packing volume and heat of sublimation of benzene (see Table XXXII) and the rotational barrier of the para-substituted ring for *s-trans*-[2.2]-metaparacyclophane (see Fig. 8) are significantly affected by the 2...112 parameters, which differ only slightly from their original values. The volume of the benzene crystal is slightly smaller than experiment. In the transition state of *s-trans*-[2.2]-metaparacyclophane, the meta-substituted ring is perpendicular to the para-substituted ring, and the hydrogen shown on the meta ring points into the para ring. Thus, the van der Waals parameter for 2...112 will significantly affect its ΔG^\ddagger , which is calculated to be 21.5 kcal/mol by MM4, somewhat higher than the experimental value of 20.6 kcal/mol.

TABLE XXIXb.
Van der Waals Parameters.

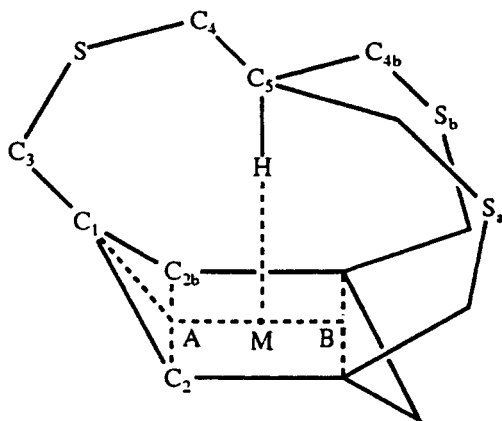
Atom	Atom Type	MM4 ϵ	MM4 Radius	Interaction	Atom Types	MM4 ϵ	MM4 Radius
C _{sp³}	1	0.037	1.96	C _{sp³} ...H	1...5	0.024	3.44
C _{sp²}	2	0.057	1.96	C _{sp²} ...H	2...5	0.048	3.20
H	5	0.017	1.64	C _{sp²} ...H	2...112	0.034	3.58
H	112	0.017	1.64				

TABLE XXX.
Hexamethylbenzene Crystal.

	Experiment	MM3	MM4
a	5.30 ± 0.02	5.26	5.29
b	8.86 ± 0.02	8.93	8.88
c	8.92 ± 0.02	8.97	8.88
α	119.3 ± 0.0	119.9	119.3
β	116.4 ± 0.0	116.2	119.7
γ	44.3 ± 0.0	46.0	44.7
vol ^a	228.5	235.8 / + 3.2%	222.4 / - 2.7%
ΔH_T^b	17.86 ± 0.5	16.83 / - 5.8%	17.04 / - 4.6%

^a See ref. 67.^b See ref. 71.**TABLE XXXI.**
Partial Geometry of
2,6,15-Trithia[3^{4,10}][7]metacyclophane (2.1b).^a

Parameter	X-ray	MM3	Δ	MM4	Δ
H ₅ —M	1.69	1.810	+0.12	1.718	+0.028
C ₅ —M	2.78	2.896	+0.12	2.809	+0.029
C ₄ —C ₅ —H ₅	105.4	105.0	-0.4	105.1	-0.3
C ₄ —C ₅ —C _{4b}	113.2	113.5	+0.3	113.4	+0.2
S—C ₄ —C ₅	116.1	114.1	-2.0	115.3	-0.8
C ₃ —S—C ₄	106.3	104.8	-1.5	105.0	-1.3
C ₁ —C ₃ —S	110.2	113.6	+3.4	112.0	+1.8
C ₃ —C ₁ —A	160.2	159.9	-0.3	161.9	+1.7
C ₁ —A—B	175.6	170.8	-4.8	171.9	-3.7

^a See ref. 70.**FIGURE 7.** Numbering for structure 2.1b.

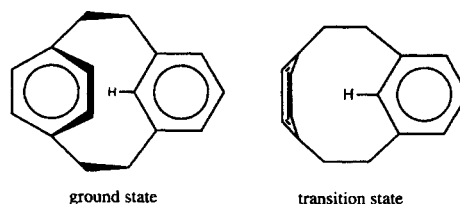
The Biphenyl Crystal

A comparison between the experimental and calculated biphenyl crystal structures is shown in Table XXXIII.

Biphenyl was determined to be planar in the crystal at 110 K by Charbonneau and Délugeard

TABLE XXXII.
Benzene Crystal.^a

	Experiment	MM3	MM4
a	7.03 ± 0.02	7.07	6.96
b	7.46 ± 0.02	7.18	7.37
c	9.67 ± 0.02	9.82	9.48
α	90.0 ± 0.3	85.5	90.0
β	90.0 ± 0.3	90.7	90.2
γ	90.0 ± 0.3	90.1	90.1
vol.	507.1	493.2 (-2.7%)	486.3 (-4.1%)
ΔH_T	10.42	10.32 (-1.0%)	10.44 (+0.2%)

^a See ref. 68.**FIGURE 8.** *s-trans*-[2.2]Metaparacyclophane.**TABLE XXXIII.**
Biphenyl Crystal.^a

	Experiment	MM3	MM4
a	7.82 ± 0.02	7.79	8.01
b	5.58 ± 0.01	5.60	5.52
c	9.44 ± 0.02	9.34	9.52
α	90.0 ± 0.0	89.3	90.4
β	94.62 ± 0.10	93.1	92.4
γ	90.0 ± 0.0	88.9	90.0
vol	410.6	406.7 (-0.9%)	419.5 (+2.2%)
ΔH_T^b	19.50 ± 0.5	18.26 (-6.4%)	18.42 (-5.5%)

^a See ref. 69.^b See ref. 73.

(CD).⁶⁹ They concluded that the libration value, L_{22} , around the long axis of biphenyl shows that the crystal is consistent with planar biphenyl conformers, and only at lower temperatures (< 40 K) could actual structural changes occur.⁷⁴ In other words, they determined that biphenyl is, at least on average, planar in the crystal structure. Whether biphenyl was indeed "planar" due to order at the molecular level or whether averaging occurred due to static or dynamic disorder remained unclear.

Lenstra and co-workers published an *ab initio* study which gives additional insight into the conformational questions concerning the biphenyl crystal.⁷⁵ Using the electrostatic crystal field (ECF-

MO) approach with a 4-21G basis set, they show that in the crystal lattice, a biphenyl molecule will adopt a dihedral angle of $\pm 27^\circ$, which is less than the approximately 44° gas phase angle, but not planar. They also found that the calculated barrier to rotation over the planar barrier is lower in the crystal, presumably due to the "flattening" effects of the neighboring biphenyl molecules. The authors claim that this reduced torsional barrier indicates that biphenyl can be undergoing dynamic disorder in the crystal (i.e., alternating between its racemic forms over time), with the average result appearing planar.⁷⁵

Lenstra et al. also mention that although thermal motion tensors such as L_{22} give precise numerical values (L_{22} was used as evidence of planarity by CD), their physical interpretations can be misleading. *Ab initio* calculated L_{22} values were determined using a rigid-body model with a pseudoharmonic potential part, which describes the dynamic disorder. The combined total computed L_{22} values were consistent with experiment at temperatures of 293, 110, and 40 K.⁷⁵

The heat of sublimation for biphenyl using MM3 and MM4 was determined in the following manner⁷⁶: First, biphenyl was packed using the planar biphenyl crystal coordinates and space group ($P2_1/a$, $Z = 2$) at 0° , 20° , and 40° orientations about the long axis of biphenyl. Second, for each case the lattice parameters were allowed to optimize on a cubic block of $3 \times 3 \times 3$ unit cells, while the molecules remained rigid. A $15 \times 15 \times 15$ block of unit cells was then constructed and the energy of the system was calculated. A center molecule was removed from the block, and the energy was recalculated, thereby determining the lattice energies. Third, the steric energy (MM3) or

enthalpy (MM4) for each biphenyl molecule was determined relative to the most stable gas phase conformer (40°). Finally, these energies were added together to give the total energy, which is equal to the heat of sublimation (ΔH_{sub}) in these cases, as shown in Tables XXXIV and XXXV. This ΔH_{sub} corresponds to the amount of energy required to pull the central molecule in the crystal lattice to an infinite distance and allow it to relax.

For MM3 (see Table XXXIV), the lattice energy gained by "flattening" biphenyl in the crystal (4.64 kcal/mol) outweighs the energy which stabilizes the twisted conformer (1.98 kcal/mol). In MM4 this trend is similar but not quite as severe. Both

TABLE XXXIV.
MM3 Energy Biphenyl Conformations in the Crystal Lattice (kcal / mol).

Model	Lattice Energy	Steric Energy	Total Energy	Heat of Sublimation
0°	-20.28	1.98	-18.26	18.26
20°	-17.65	0.71	-16.94	16.94
40°	-15.64	0.00	-15.64	15.64

TABLE XXXV.
MM4 Energy Biphenyl Conformations in the Crystal Lattice (kcal / mol).

Model	Lattice Energy	Enthalpy ^a	Total Energy	Heat of Sublimation
0°	-20.34	1.92	-17.87	18.42
40°	-16.52	0.00	-16.52	16.52

^a The enthalpies are calculated from the planar and minimum energy structures, respectively.

TABLE XXXVI.
Dipole Moments of Conjugated Hydrocarbons (Debye).

	Expt. ^a	π	MM3 σ	Total	π	MM4 σ	Total
trans-1,3-Pentadiene	0.585	0.001	0.285	0.284	0.000	0.336	0.336
cis-1,3-Pentadiene	0.500	0.012	0.251	0.247	0.012	0.306	0.303
trans-Isoprene	0.15, 0.38	0.069	0.332	0.26	0.016	0.304	0.306
Cyclopentadiene	0.419	0.105	0.318	0.214	0.104	0.554	0.450
1,3-Cyclohexadiene	0.437	0.077	0.520	0.443	0.078	0.614	0.536
Toluene	0.37	0.004	0.293	0.289	0.004	0.346	0.342
Fulvene	0.44	0.237	0.012	0.23	0.232	0.013	0.218
Dimethylfulvene	1.48	0.253	0.338	0.591	0.231	0.387	0.618
Azulene	0.796	0.991	0.115	1.206	0.908	0.119	1.027

^a See ref. 78. All experimental results are gas phase, except for dimethylfulvene (benzene).

methods predict that biphenyl is planar in the crystal lattice rather than twisted 42° .

DIPOLE MOMENTS

The dipole parameters are virtually the same for MM4 as MM3, with the bond dipole for $C_{sp^3}-C_{sp^2}$

assigned as 0.95 D (0.90 D MM3) and $H-C_{sp^2}$ having a value of 0.60 D, the same as in MM3. The dipole parameters are important not only for calculating dipole moments and energies, but also for determining crystal packing forces. All of the experimental dipole moments, with the exception of cyclopentadiene, were determined from dielectric

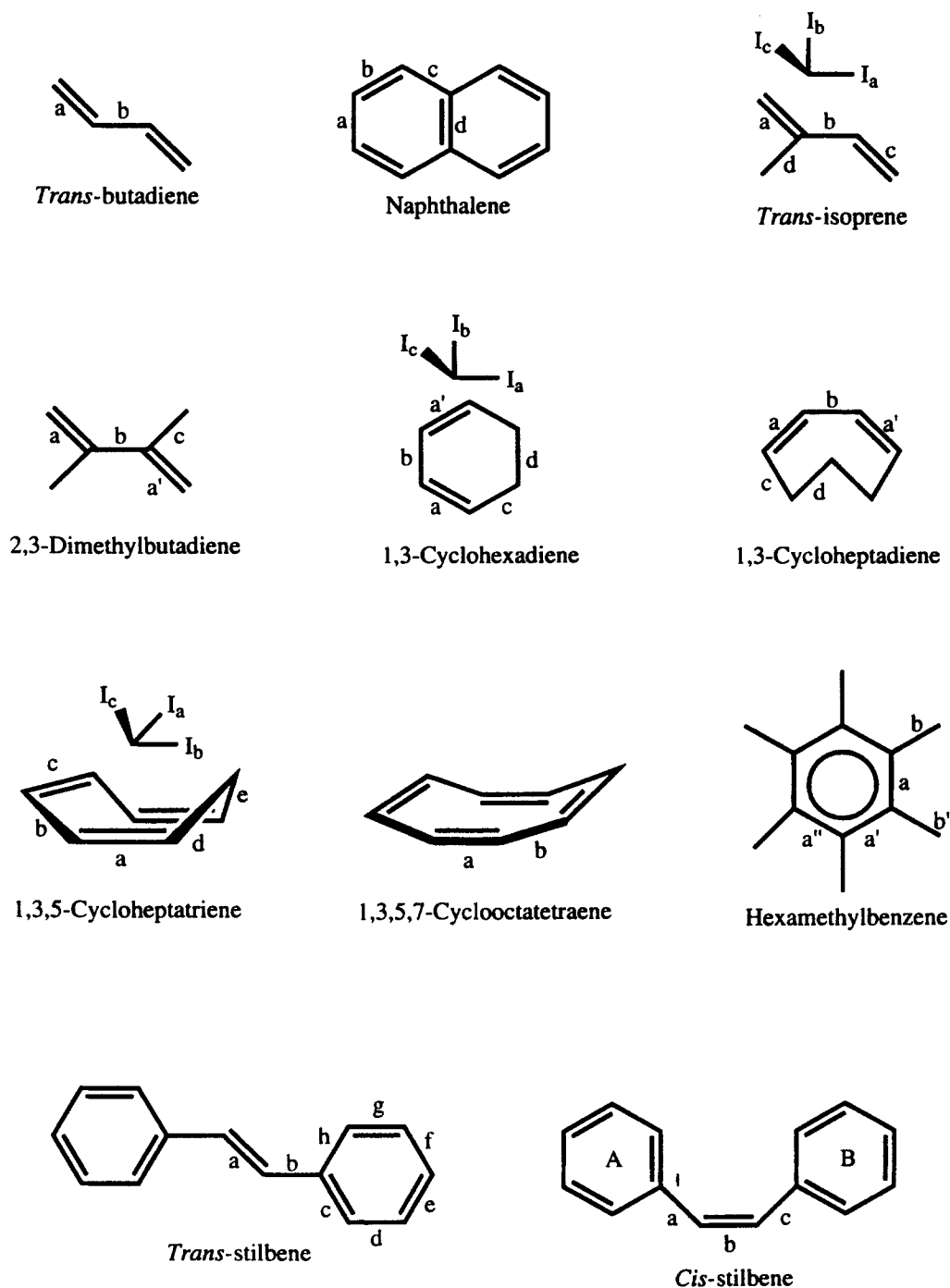


FIGURE 9a. Structures and labeling for conjugated hydrocarbons.

constant measurements (see Table XXXVI). Cyclopentadiene's dipole moment was determined from a microwave experiment (Stark effect). Further discussion of the conjugated molecule dipole moments is given elsewhere.⁷⁷

GEOMETRIES

Since these quantities were already fit well with MM3, not much improvement was expected or seen for MM4. Comparisons of MM3 and MM4 results and experimental structural data for 28

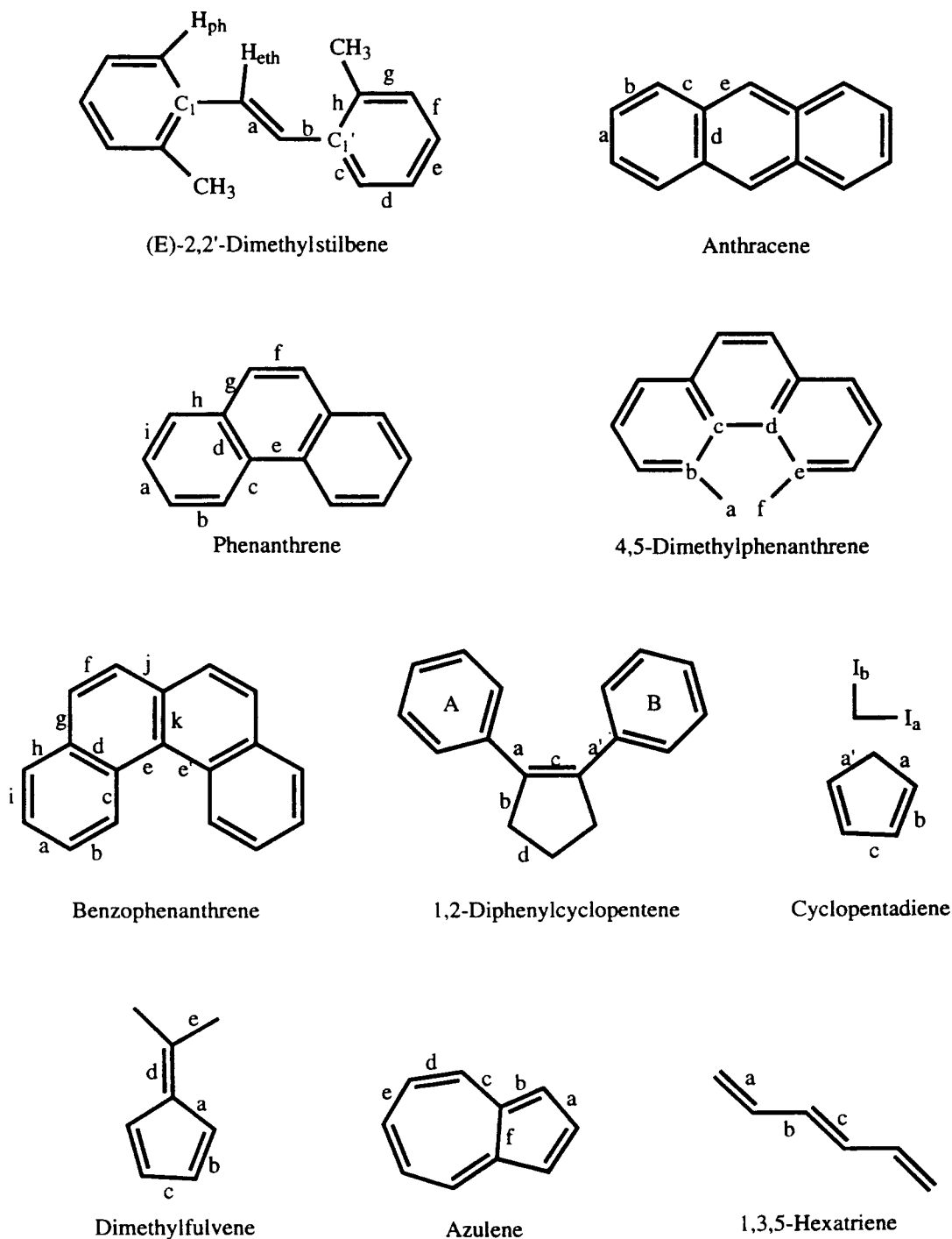


FIGURE 9b. Structures and labeling for conjugated hydrocarbons.

conjugated hydrocarbons have been compiled, including bond lengths, bond angles, and torsional angles. These structures are shown in Figure 9. The results for ethylene, benzene, and *trans*-butadiene are shown in Table XXXVII. A few other molecules

are shown in Tables XXXVIII–XLIV. Since these results are similar, and most of these compounds have been discussed previously,⁴ the results for most of the remaining structures are given in Tables XLV–LXI in Supplementary Material.

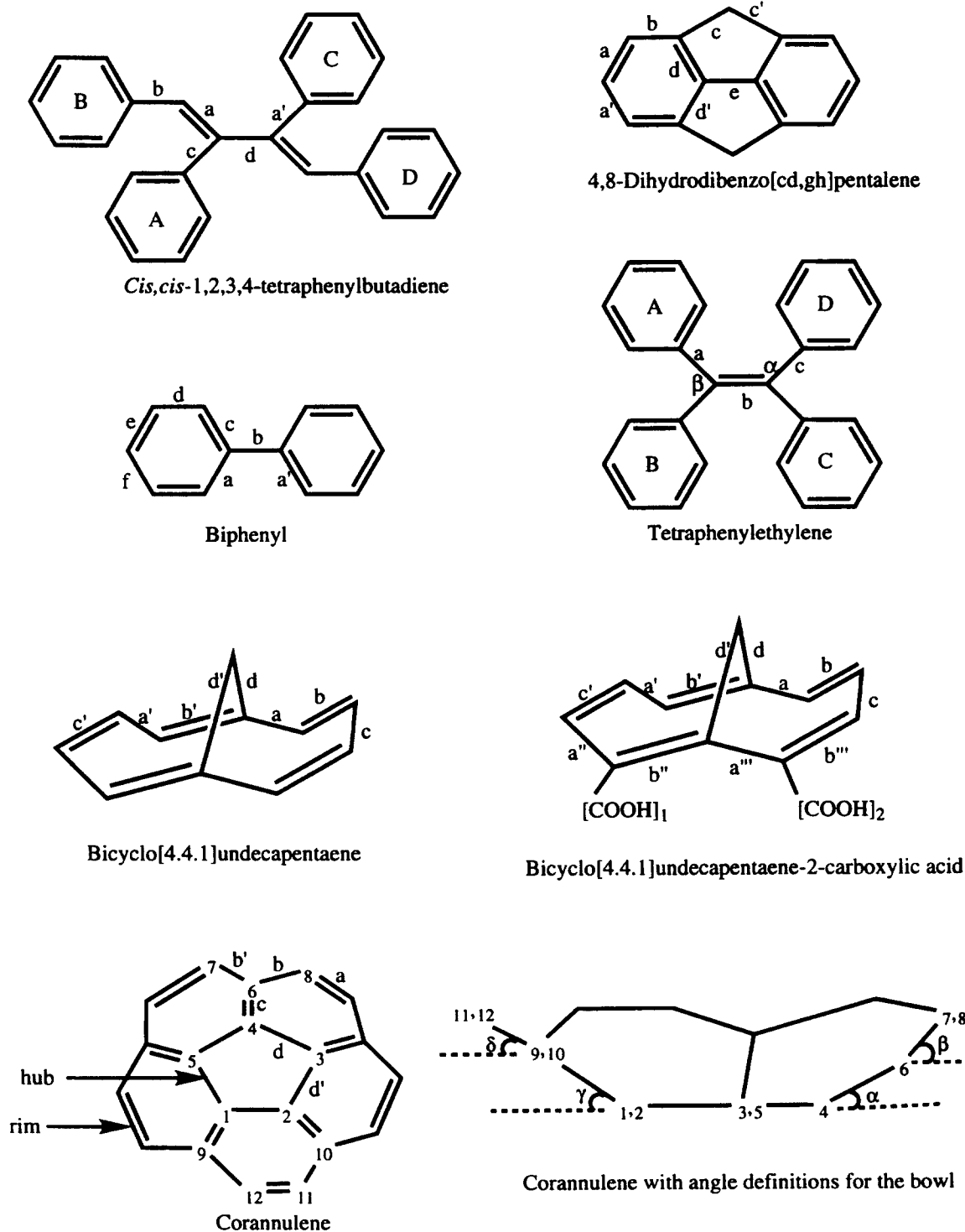


FIGURE 9c. Structures and labeling for conjugated hydrocarbons.

TABLE XXXVII.
Ethylene, Benzene, and *trans*-Butadiene.^a

	Ref.	Bond	Expt.	MM4	Δ	MM3	Δ
Ethylene	82	a	1.337 ± 0.001	1.337	0.000	1.337	0.000
Benzene	83	a	1.399 ± 0.001	1.397	-0.002	1.397	-0.002
<i>Trans</i> -butadiene	11	a	1.344 ± 0.001	1.343	-0.001	1.344	0.000
		b	1.467 ± 0.001	1.469	+0.002	1.468	+0.001
		ab	122.9 ± 0.5	123.0	+0.1	122.4	-0.5

^a All structures are electron diffraction (ED), r_g bond lengths.**TABLE XXXVIII.**
***trans*-Isoprene.^a**

Bond / Angle	Expt.	MM4	Δ	MM3	Δ
a	1.340 ± 0.001	1.347	+0.007	1.350	+0.010
b	1.463 ± 0.001	1.479	+0.016	1.475	+0.012
c	1.340 ± 0.002	1.344	+0.004	1.345	+0.005
d	1.512 ± 0.002	1.512	0.000	1.511	-0.001
average	1.414	1.421	+0.007	1.421	+0.007
ab	121.4 ± 0.3	120.0	-1.4	119.7	-1.7
bc	127.3 ± 0.3	123.9	-3.4	124.0	-3.3
ad	121.0 ± 0.2	120.1	-0.9	119.5	-1.5

^a Reference 84, ED, r_α bond lengths.**TABLE XXXIX.**
***trans*-2,3-Dimethyl-1,3-butadiene.^a**

Bond / Angle	Expt. (r_a)	Expt. (r_g)	MM4	Δ (r_g)	MM3	Δ (r_g)
a	1.349	1.351	1.348	-0.003	1.349	-0.002
b	1.491	1.493	1.492	-0.001	1.487	-0.006
c	1.511	1.513	1.513	0.000	1.512	-0.001
average	1.442	1.444	1.443	-0.001	1.441	-0.003
ab	121.98		121.0	-1.0	121.1	-0.9
bc	117.87		119.8	+1.9	120.2	+2.3
aba'	180.0		180	0	160	-20

^a Reference 85, ED, r_g bond lengths (corrected from r_a as explained in text).**TABLE XL.**
Cyclopentadiene.^a

Bond	Expt.	MM4	Δ	MM3	Δ
a	1.509 ± 0.002	1.520	+0.011	1.521	+0.012
b	1.342 ± 0.003	1.347	+0.005	1.347	+0.005
c	1.469 ± 0.002	1.465	-0.004	1.473	+0.004
av	1.434	1.440	+0.006	1.442	+0.008
aa'	102.8	102.3	-0.5	101.8	-1.0
bc	109.4	109.6	+0.2	109.3	-0.1

^a Reference 86, microwave (MW), r_s bond lengths.

Bicyclo[4.4.1]-undecapentaene and (E)-stilbene will be discussed in some detail, and the results for these compounds are given in Tables LXII and LXIII, respectively.

Bicyclo[4.4.1]undecapentaene

A room temperature X-ray crystal structure exists for 1,6-methanocyclopentaene-2-carboxylic acid

(bicyclo[4.4.1]undecapentaene-2-carboxylic acid).⁷⁹ Since MM4 parameters for the carboxylic acid part of the molecule have not yet been determined, the MM4 structure of bicyclo[4.4.1]undecapentaene (without the carboxylic acid group) is compared to the X-ray results.

Optimization of this structure posed some problems. The block-diagonalization method converged somewhat, but not to anywhere near the

TABLE XLI.
1,3-Cyclohexadiene.^a

Bond / Angle	Expt./ σ (r_a)	Expt. (r_g)	MM4	Δ (r_g)	MM3	Δ (r_g)
a	1.350 \pm 0.004	1.352	1.346	-0.006	1.345	-0.007
b	1.468 \pm 0.014	1.470	1.471	+0.001	1.465	-0.005
c	1.523 \pm 0.016	1.525	1.511	-0.014	1.510	-0.015
d	1.534 \pm 0.020	1.536	1.544	+0.008	1.540	+0.004
av	1.458 \pm 0.012	1.460	1.455	-0.005	1.453	-0.007
ab	120.1	—	120.3	+0.2	120.5	+0.4
ac	120.1	—	120.9	+0.8	120.9	+0.8
cd	110.7	—	111.4	+0.7	111.8	+1.1
aba'	18.3	—	13.0	-5.3	13.3	-5.0

^a Reference 87, ED, r_g bond lengths (corrected from r_a as explained in text).

TABLE XLII.
1,3,5-Cycloheptatriene.^a

Bond / Angle	Expt.	MM4 ^b	Δ	MM4 ^c	Δ	MM3	Δ
a	1.356	1.346	-0.010	1.346	-0.010	1.345	-0.011
b	1.446	1.467	+0.021	1.467	+0.021	1.461	+0.015
c	—	1.353	—	1.353	—	1.355	—
d	1.505	1.511	+0.006	1.511	+0.006	1.509	+0.004
ab	127.2	124.8	-2.4	124.7	-2.5	125.4	-1.8
bc	119.8	126.9	+7.1	126.8	+7.0	126.9	+7.1
ad	121.8	123.6	+1.8	123.5	+1.7	124.9	+3.1
de	—	112.1	—	111.2	—	—	—

^a Reference 88, ED, r_g bond lengths.

^b This geometry is obtained from optimization by the MM4 program directly.

^c This geometry is obtained when the $C_{sp^2}-C_{sp^3}-C_{sp^2}$ angle is manually lowered to 111.0° (and the energy for the structure is calculated with the regular parameters); see moments of inertia discussion for 1,3,5-cycloheptatriene.

TABLE XLIII.
Naphthalene.^a

Bond	Expt. (r_a)	Expt. (r_g)	MM4	Δ (r_g)	MM3	Δ (r_g)
a	1.417 \pm 0.004	1.419	1.422	+0.003	1.421	+0.002
b	1.38 \pm 0.002	1.383	1.373	-0.010	1.374	-0.009
c	1.422 \pm 0.003	1.424	1.429	+0.005	1.429	+0.006
d	1.412 \pm 0.008	1.414	1.411	-0.003	1.412	-0.002
av	1.405 \pm 0.004	1.407	1.406	0.001	1.406	-0.001
cd	119.5	—	119.2	-0.3	119.3	-0.2

^a Reference 89, ED, r_g bond lengths (corrected from r_a as explained in text).

cutoffs for geometry or energy optimization. Full-matrix optimization would seemingly result in convergence, but reoptimizing the resultant geometry led to a further reduction in energy. This occurred because although the geometry was optimized after the full-matrix calculation, the electronic energy was not necessarily consistent with the new geometry. Thus, another VESCF calculation really was needed after the full-matrix calculation until self-consistency could be reached for both the electronic and steric energy components. Therefore, a significant number of reoptimizations (8–12) were required for the energy to converge to within 0.05 kcal/mol. Thus, MM4 was modified so that it now repeats the VESCF calculation/optimization sequence until the rms force drops below 0.02 kcal/mol-Å on the first iteration of the full-matrix optimization. This change will also be im-

plemented in MM3(96) and later versions, but with older versions of MM3, the user must rerun the optimization until satisfied.

This geometry is presented in Table LXIIa (also see Fig. 9). The X-ray results are presented as averages of "equivalent" bond lengths and angles (C_{2v} symmetry assumed) to compare with the MM3 and MM4 structures of bicyclo[4.4.1]undecapentaene.

The MM4 bond lengths have alternating single- and double-bond character, as evidenced by the large differences in bond lengths. The actual geometry is probably an average of the two Kekule forms of the molecule and has more equal bond lengths. If electron correlation could be introduced into the MM4 calculation, the bonds would probably become more aromatic (i.e., more of an average of the single/double bond character). Interpreting

TABLE XLIV.
Biphenyl (twisted).^a

Bond / Angle	Expt.	Expt. (r_g)	MM4	Δ (r_g)	MM3	Δ (r_g)
a	1.403 \pm 0.004	1.405	1.402	-0.003	1.403	-0.002
b	1.503 \pm 0.004	1.505	1.486	-0.019	1.488	-0.017
d	1.395 \pm 0.006	1.397	1.396	-0.001	1.396	-0.001
e	1.396 \pm 0.008	1.398	1.395	-0.003	1.396	-0.002
av	1.406	1.408	1.405	-0.003	1.405	-0.003
ac	119.4		118.6	-0.8	118.7	-0.7
cd	119.9		120.7	+0.8	120.6	+0.7
de	120.9		120.1	-0.8	120.1	-0.8
ef	119.0		119.7	+0.7	119.8	+0.8
aba'	44.4 \pm 1.2		41.5	-2.9	46.1	+1.7

^a Reference 90, ED, r_g bond lengths (corrected from r_a as explained in text).

TABLE LXIIa.
Bicyclo[4.4.1]undecapentaene.^a

Bond / Angle	Expt. ^b	MM4 ^c	Δ	MM3 ^c	Δ
a _{av}	1.392	1.441	+0.049	1.462	+0.070
b _{av}	1.401	1.374	-0.027	1.360	-0.003
c _{av}	1.415	1.430	+0.015	1.425	+0.010
d	1.477	1.484	+0.007	1.491	+0.014
ab _{av}	122.3	120.8	-1.5	122.1	+0.1
bc/a'c'	127.7	128.9	+1.2	127.2	-0.5
ab' _{av}	127.4	129.2	+1.6	124.1	-3.6
ad/b'd	116.1	115.3	-0.7	117.3	+1.2
dd'	99.6	102.4	+2.8	101.2	+1.6

^a Reference 79, X-ray, room temperature.

^b Experimental data from bicyclo[4.4.1]undecapentaene-2-carboxylic acid ("equivalent" bond lengths and angles are averaged; C_{2v} symmetry assumed).

^c MM4 results are for a structure without the carboxylic acid group after repeated reoptimizations (convergence within 0.05 kcal/mol); MM4 "equivalent" bond lengths and angles are averaged as for the experimental results for structure.

TABLE LXIib.
Bicyclo[4.4.1]undecapentaene-2-Carboxylic Acid.^a

Bond _{av} ^b	Expt. ^c	MM4 ^d	Δ	Angle	Expt. ^c	MM4 ^d	Δ
a / b'	1.405	1.405	+0.000	ab	122.3	121.1	-1.2
a''' / b''	1.414	1.408	-0.006	a'b'	122.7	120.7	-2.5
a' / b	1.383	1.408	+0.025	bc	126.7	128.8	+2.1
a' / b'''	1.392	1.410	+0.018	a'c'	126.1	128.2	+2.1
c / c'	1.415	1.428	+0.013	ab'	125.8	128.5	+2.7
d / d'	1.477	1.486	+0.009	a'''b''	128.9	129.6	+0.7
				ad	117.0	115.8	-1.2
				b'd	116.8	115.6	-1.2
				dd'	99.6	101.7	+2.1

^a Reference 79, X-ray, room temperature.^b The X-ray / MM4 bond lengths are averaged about a plane of symmetry through atoms comprising angle dd'.^c Experimental data from bicyclo[4.4.1]undecapentaene-2-carboxylic acid.^d MM4 results are from an average of the two structures with the carboxylic groups in each of the two positions in Figure 9c after repeated reoptimizations (convergence within 0.05 kcal/mol).

the angles is somewhat more difficult, especially because of the carboxylate group. The angles vary from the experimental values by ± 1 – 2.5° for MM4 and are better on average for MM3.⁴ The data originally published for MM3 were not completely optimized for the reason mentioned earlier, although this was not realized at the time. The MM3 results (after full-matrix reoptimization until convergence to within 0.05 kcal/mol) are also presented in Table LXIib.

The $C_{sp^3}-C_{sp^2}-C_{sp^3}$ angle is much closer to experiment for MM3 than for MM4. This may be in part due to a relatively large bending constant (0.75 mdyn/Å) in MM4, which was chosen to better fit norbornadiene moments of inertia and

the barrelene geometry. A reduction in this force parameter would improve this angle for MM4 but could lead to other errors, so it was decided to leave the current value in place.

An average of two MM4 structures with the carboxylic acid group at the 2 position (relative to the bonds labeled c and c' in Fig. 9c) was computed and compared to explicit bond angles and bond lengths that were averaged about a plane of symmetry through atoms comprising angle dd' (see Table LXIib and Fig. 9c) from the X-ray structure. Including the carboxylic acid group (with estimated parameters) leads to changes in bond lengths and angles (relative to the MM4 structure without this group), including a reduction in the

TABLE LXIII.
trans-Stilbene.^a

Bond / Angle	Expt.	MM4	Δ	MM3	Δ
a	1.338	1.350	+0.012	1.355	+0.017
b	1.473	1.477	+0.004	1.477	+0.004
c	1.406	1.405	-0.001	1.410	+0.004
d	1.393	1.395	+0.002	1.395	+0.002
e	1.394	1.395	0.001	1.397	+0.003
f	1.391	1.395	+0.004	1.394	+0.003
g	1.390	1.396	+0.006	1.397	+0.007
h	1.402	1.405	+0.003	1.407	+0.005
av	1.402	1.406	+0.004	1.407	+0.005
ab	126.0	124.8	-1.2	125.2	-0.8
bh	123.7	122.5	-1.2	123.0	-0.7
bc	118.2	119.3	+1.1	118.9	+0.7
ch	118.1	118.2	+0.1	118.1	0.0
abh	5.2	17.4	+12.4	1.7	-3.5

^a Reference 81c, X-ray, 160°C.

$C_{sp^3}-C_{sp^2}-C_{sp^3}$ angle of about 0.6° . Since the carboxylic acid group is treated approximately, direct comparison to this structure may be misleading.

(E)-Stilbene

Room temperature X-ray crystal structures reported for a series of substituted (E)-stilbenes have been determined to have unusually short central $C=C$ bond distances of 1.283–1.327 Å.⁸⁰ The experimental $C=C$ distance for ethylene is 1.337 Å. However, X-ray structures for these same compounds exhibit much longer bond lengths at lower temperatures (see Tables LXIII and LXIV in the Supplementary Material, and Fig. 9a).⁸¹ At approximately 120°C, this same bond length increases to 1.321–1.342 Å. Furthermore, the bond angle $C=C-C_{ph}$ decreases significantly with the decrease in temperature. IR analysis shows no change in the $C=C$ ethylene-type stretching frequency, regardless of temperature. Furthermore, UV and NMR studies do not indicate that this bond length changes with temperature.

Ogawa and co-workers use the "dynamical disorder" model to explain these findings for X-ray structures.⁸⁰ The long axes of the probability density function (pdf) ellipsoids of the ethylene carbons are perpendicular to the molecular plane of the molecule. It was suggested that this particular disorder is due to torsional vibration of the $C-Ph$ bonds. During this type of vibration, the benzene rings remain relatively stationary while the ethylene unit undergoes significant disorder. In effect, there is an interconversion of enantiomers of (E)-stilbene, and the ethylene $C=C$ bonds (and

$C=C-C_{ph}$ angles) of each enantiomer cross each other. This crossing is detected as a structural average of the two conformers by the X-ray crystallographic method, and this results in the appearance of shorter $C=C$ bond lengths and larger $C=C-C_{ph}$ angles. At lower temperatures, there is much less disorder due to the reduced amplitudes of the aforementioned vibrations, and the $C=C$ bond lengths approach their "true" values and are comparable to the MM4 values (see Table LXIII and also Table LXIV in the Supplementary Material for the 2,2'-dimethyl derivative).

MOMENTS OF INERTIA

For conjugated molecules, the MM4 calculated moments of inertia are slightly better than the MM3 ones. The deviations from experiment could in part be due to the lack of bond order dependence for the bending parameters. The largest errors occur for 1,3,5-cycloheptatriene, which is discussed next. The moments of inertia for three additional conjugated hydrocarbons are given in Tables LXV–LXVIII (Supplementary Material), and their orientations are shown in Figure 9. All of the calculated moments are well within 1% of the experimental values, except for cycloheptatriene.

1,3,5-Cycloheptatriene

Trying to improve its moments of inertia here leads to problems with the energies of molecules involving $C_{sp^2}-C_{sp^3}-C_{sp^2}(-C_{sp^2})$ -type parameters. The minimum energy structure is now more boatlike than with MM3 (see I_a value), and consequently the MM4 energy barrier is calculated much

TABLE LXVIII.
1,3,5-Cycloheptatriene.^a

	I_a	%	I_b	%	I_c	%
Exp.	22.71		22.85		41.29	
MM3	23.10	+1.7	23.29	+1.9	43.31	+4.8
MM4 (r_g) ^b	22.959	+1.1	23.421	+2.5	42.971	+4.1
MM4 (r_z) ^b	22.857	+0.65	23.326	+2.1	42.811	+3.7
MM4 (r_g) ^c	22.975	+1.2	23.341	+2.1	42.785	+3.6
MM4 (r_z) ^{c,d}	22.873	+0.72	23.246	+1.7	42.625	+3.2

^a See ref. 91; units are $10^{-39} \text{ g} \cdot \text{cm}^2$.

^b These moments are obtained from geometries optimized by the MM4 program directly.

^c Geometry corresponding to calculated energy minimum.

^d The r_z moments of inertia for the manually optimized structure cannot be calculated directly and thus are estimated using the ratio from the results obtained by direct optimization $[r_g/r_z]_{\text{dir opt}} = [r_g/r_z]_{\text{hand opt}}$. This structure is not considered a minimum by the force field, and thus the vibrational amplitude contribution required for calculating r_z bond lengths and moments of inertia cannot be computed.

closer to experiment (see Conformational Analysis section). However, the bond angles are still calculated poorly by MM4 (see Table LXVIII), which is reflected in the large deviations for I_b and I_c .

Again, homoconjugation in this ring may be causing some of the problem. One might expect the p_x orbitals on the C_{sp^2} carbons (bonded to the C_{sp^3} carbon) to overlap (bonding), resulting in a closer approach of the C_{sp^2} carbons. This is not fully accounted for automatically by the MM4 program (as bond distances between nonbonded atoms are not optimized using the bond order-bond length relationship). Manually reducing the $C_{sp^2}-C_{sp^3}-C_{sp^2}$ angle and then recalculating the energy in an iterative fashion until the energy minimum is located gave a structure with the I_b and I_c moments of inertia reduced by about 0.5%, compared to these values obtained from straight optimization by the MM4 program (see Table LXVIII).

CONCLUSIONS

The MM4 force field is the successor to MM3. Existing MM3 equations have been modified and/or extended. Additional cross-terms have also been added to the force field. These improvements were necessary in order to resolve existing discrepancies between MM3 and experiment and to account for new or reinterpreted experimental data that were not available during development of MM3. Major improvements result for vibrational frequencies, and those are detailed in the following article.³

Conformational energy differences and rotational barriers are calculated better on average by MM4. This is due in part to comparing calculated MM4 quantities (steric energies, enthalpies, and free energies) directly with the data that are available for a particular compound (thermodynamic measurements, *ab initio*, variable-temperature IR, NMR, etc.). Most energy barriers and differences are calculated to within experimental error by MM4. Also, the torsional potential has been extended to include a V4 term for conjugated hydrocarbons (and alkenes). Thus, the ethylene- and diene-type rotational barriers and torsional frequencies can be better fit simultaneously.

The overall rms error for heats of formation calculated by MM3 and MM4 are similar, but the weighted rms is slightly improved for MM4. The overall weighted rms for 35 alkenes and 57 conju-

gated hydrocarbons is 0.47 kcal/mol (MM3 is 0.53 kcal/mol) for the same group of compounds.

The torsion-torsion term lowers the relative energies of more highly aromatic (nearly equal bond orders) compounds relative to less conjugated (alternating bond orders) ones. This results in some improvement in the heats of formation and vibrational frequencies. The torsion-bend cross-term helps to improve the moments of inertia for compounds discussed in the previous articles.

The atom type numbers for hydrogens attached to carbons have been expanded. In MM3, atom type 5 was assigned to hydrogens attached to either a C_{sp^2} or C_{sp^3} carbon. An atom type of 112 is now assigned to hydrogens attached to C_{sp^2} carbons, while type 5 remains for hydrogens attached to C_{sp^3} carbons. The (type 2) carbon/hydrogen van der Waals parameters are no longer the sum of each individual radius and the square root of the product of the individual epsilons. Instead, the van der Waals radius and epsilon for C_{sp^3}/H were adjusted to be lower and higher, respectively, than the combination-rule values. This allows for the modification of van der Waals parameters in order simultaneously to fit crystal packing data and *in*-cyclophane stretching frequencies.

The MM4 program will calculate r_e , r_a , r_α , r_s , and r_z values. Thus moments of inertia can be computed from the r_z bond lengths, which allows for a more direct comparison with microwave values.

Supplementary Material

The package of Supplementary Material referred to in the text (27 Tables of MM4 results) is available from the authors upon request.

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